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Deposition of Nickel and Cobalt by Chemical Reduction

By Abner Brenner and Grace Riddell

A process has been developed for depositing nickel and cobalt from hot solutions of hypophosphite without the use of current. The reduction of metal occurs only on certain catalytic metal surfaces. By specific pretreatments, the adhesion of the deposits can be improved and by other pretreatments, the reduction can be induced on noncatalytic surfaces. The reduction can be inhibited completely by the presence of certain ions in the plating solution or by the catalytic metal surface becoming inactive. The possible mechanism of the reaction and the factors affecting the rate of deposition are discussed. The deposits produced by this process are sound, hard, and of good quality.

I. Introduction

Since the publication of a report by the authors [1] of a process for depositing nickel by chemical reduction, additional information has been obtained that broadens the operating conditions and the applications of this process. The first paper described the deposition of nickel from an ammoniacal solution containing hypophosphite. The process has been extended to include the deposition of nickel from acid solutions and of cobalt and cobalt-nickel alloys from ammoniacal solutions.

The process involves the reducing action of hypophosphites in a solution of nickel or cobalt at 90° C or above in the presence of certain catalytic metals. The reactions can be expressed by the following equations:

$$NiCl_2+NaH_2PO_2+H_2O\rightarrow Ni+2HCl+NaH_2PO_3 \quad (1)$$

or

$$NaH_2PO_2+H_2O\rightarrow NaH_2PO_3+H_2. \quad (2)$$

The hypophosphite undergoes oxidation, and the nickel is reduced. Both of these components must be added at intervals to make the deposition continuous.

An interesting feature of the process is that the deposition of nickel or cobalt occurs only on certain metallic surfaces that are immersed in the hot solution, and that deposits are not usually obtained on the glass vessels. No electric current is involved in the deposition. It is suggested that this process be designated as "electroless nickel plating" and "electroless cobalt plating".

[1] Abner Brenner and Grace E. Riddell, J. Research NBS **37**, 31 (1946) RP1725; AES Annual Proceedings, p. 23 (1946).

II. Composition and Operating Characteristics of Solutions

1. Nickel

(a) Alkaline Solutions

This subject, treated in the previous paper, will be reviewed briefly for completeness. The most satisfactory alkaline solutions are ammoniacal, and contain citrates, ammonium salts, hypophosphites, and nickel salts. A typical bath is composed of:

	g/liter
Nickel chloride	30
Sodium hypophosphite	10
Ammonium chloride	50
Sodium citrate	100
Ammonium hydroxide to a pH of 8 to 10	

Such a solution deposits nickel at the rate of 0.0002 to 0.0003 in. (0.005 to 0.008 mm) per hour.

As previously indicated, the rate of deposition depends upon the composition of the solution and is approximately proportional to the concentration of the hypophosphite, as shown in table 1. Varying the concentration of nickel salts within the limits shown produces no appreciable change in

the rate of deposition. Other factors, such as the concentration of organic salt, effect the rate of deposition to a smaller degree.

TABLE 1. *Effect of bath composition on rate of deposition*

Concentration	Rate of deposition per hour	
SODIUM HYPOPHOSPHITE		
g/liter	*in.*×10^{-4}	*mm*×10^{-3}
2	0.3	8
4	.6	15
10	2.4	61
50	7.5	165
NICKEL		
3.8	2.2	55
7.5	2.6	66
15	3.0	76

Table 2 indicates that the rate of deposition increases rapidly with temperature. This effect of temperature applies also to the acid-nickel solution and the alkaline cobalt solution, which will be discussed later.

TABLE 2. *Effect of temperature on rate of deposition*

Temperature	Thickness per 30 minutes	
° C.	*in.*×10^{-4}	*mm*×10^{-3}
54	0.155	0.39
68	.38	.96
78	.64	1.63
87	.94	2.4
92	1.1	2.8

If additions of hypophosphite are made at suitable intervals, the useful life of such a solution is relatively long. In a 1-liter bath, the equivalent of an area of 40 square decimeters was plated for 1 hour before the bath became inefficient. (This is equivalent to about 16 square feet for 1 hour in a 1-gallon bath). If the nickel concentration had been constant, and the solution had been filtered at intervals, the useful life of the solution would have been still greater.

(b) Acid Solutions

The alkaline-nickel solutions yield good, sound deposits, but in practice, their use is inconvenient and uneconomical, because at the high temperature of operation, there is a rapid loss of ammonia, and the fumes are disagreeable.

Earlier attempts to prepare an acid-nickel solution for electroless plating were unsuccessful. More recently an acid-nickel solution was formulated that overcomes the disadvantages of the alkaline solution. When the acid solution is used at elevated temperatures, no fumes or loss of constituents by vaporization occurs. The solution is more easily controlled and the deposits are produced at a faster rate than from alkaline solutions.

The proposed acid-nickel solutions differ from the alkaline-nickel solution in composition as well as in pH. Typical bath compositions are given in table 3.

TABLE 3. *Composition of the acid-nickel solutions*

	Bath			
	I	II	III	IV
	g/liter	*g/liter*	*g/liter*	*g/liter*
Nickel chloride, $NiCl_2.6H_2O$	30	30	30	
Nickel sulfate, $NiSO_4.7H_2O$				
Sodium hypophosphite, $NaH_2PO_2.H_2O$	10	10	10	
Sodium hydroxyacetate, $NaC_2H_3O_3$	50	10		
Sodium acetate, $NaC_2H_3O_2.3H_2O$				
Sodium citrate, $Na^3C_6H_5O_7.5\frac{1}{2}\ H_2O$			10	
Rate of deposition:				
Millimeters per hour	0.015	0.013	0.005	0.02
Inches per hour	.0006	.0005	.0002	.00
Appearance of deposit	Semi-bright	Semi-bright	Semi-bright	Rough dull
pH	4 to 6	4 to 6	4 to 6	4 to 6

At a pH of 5, nickel deposition will occur in a solution containing only soluble nickel salts and sodium hypophosphite. The reaction is vigorous and the reduction of nickel is very rapid. Without any regulation of the pH, the latter drops rapidly and at a pH of 1 to 2, the rate of deposition is low. In order to prevent the rapid drop in pH, salts of organic acids are added as buffers, the most satisfactory being sodium acetate and salts of certain hydroxycarboxylic acids. These buffers maintain a high rate of nickel deposition, and the hydroxycarboxylic salts prevent precipitation of basic nickel salts.

To obtain the best deposits from a solution buffered by sodium acetate, its concentration must be carefully regulated. The data in table 4 indicate that large variations in the rate of nickel deposition results from changes in the acetate concentration. The rate of deposition reaches a maximum in the nickel-chloride bath with an acetate content of 2.5 g/liter; and in the nickel-

sulfate bath, of 4.3 g/liter. The acetate can be added as barium, sodium, nickel, or other soluble salt. The acetate bath has the disadvantage of becoming turbid with use and of producing deposits that are dull and rough.

TABLE 4. *Effect of acetate concentration on rate of deposition*

Bath composition	Acetate radical	Thickness of deposit in 1 hr	
	g/liter	*in.*×10⁻⁴	*mm*
Nickel sulfate, 35 g/liter, and sodium hypophosphite, 10 g/liter.	2.0	7.5	0.02
	4.3	10.0	.025
	6.5	4.0	.01
Nickel chloride, 30 g/liter, and sodium hypophosphite, 10 g/liter.	1.0	2.0	.005
	2.5	6.0	.015
	6.5	1.0	.0026
	20.0	0.6	.0016

Certain hydroxycarboxylic acids, such as hydroxyacetic and citric acids, yield good rates of nickel deposition and likewise prevent precipitation of basic nickel salts, which cause rough deposits. Citrates produce deposits of good physical properties, but the rate of deposition is lower than from hydroxyacetate or acetate solutions. Tartaric, malic, gluconic, and formic acids are unsatisfactory because negligible amounts of nickel are deposited in their presence. Table 5 indicates that 50 g/liter and 100 g/liter of sodium hydroxyacetate give the highest rates of deposition, respectively, for the nickel-sulfate and nickel

TABLE 5. *Effect of the concentration of hydroxyacetate on rate of deposition*

Bath composition	Na hydroxyacetate	Thickness of deposit in 1 hr	
	g/liter	*in.*×10⁻⁴	*mm*
Nickel sulfate, 35 g/liter, and sodium hypophosphite, 10 g/liter.	10	1.0	0.003
	50	4.0	.01
	100	3.3	.008
	200	2.8	.007
Nickel chloride, 30 g/liter, sodium hypophosphite, 10 g/liter.	10	4.0	.01
	50	6.0	.015
	100	7.0	.018

chloride solutions. The concentrations of the other components may vary considerably. The nickel content may vary from 3 to 50 g/liter without appreciably altering the rate of deposition, but with a nickel content of 100 g/liter, the rate of deposition is somewhat decreased.

Sodium hypophosphite can be used in concentrations from 10 to 100 g/liter without appreciably affecting the rate of the process. This is in contrast to the behavior of the alkaline solution, in which the rate of deposition is nearly proportional to the concentration of hypophosphite.

The preferred pH range is from 4 to 6.5. As made up, the solutions have a pH of about 6 and no pH adjustment is required for a new bath. However, with long use, the pH drops slowly and, for continued rapid deposition, additions of a dilute hydroxide solution should be made at regular intervals. Because of the action of the buffer, frequent additions of hydroxide are not necessary. The alkaline solution used for the pH regulation should be dilute, so that the additions will not cause local precipitation of nickel compounds. Sodium and potassium hydroxide are used in preference to ammonium hydroxide, because large concentration of ammonium salts tend to lower the rate of the reaction.

The yield or efficiency of the reaction, calculated on the hypophosphite was determined by weighing the amount of nickel deposited on (1) a relatively large metal surface in a small volume of solution (i. e., 0.5. dm^2/100 ml) and (2) a relatively small metal surface in a large volume of solution. (i. e., 0.5 dm^2/liter) Under the first conditions, the average efficiency is 37 percent, i. e. about 2 g of nickel is reduced by 10 g of sodium hypophosphite. In the second procedure, the efficiency is only about 20 percent. Although both alkaline and acid solutions have about the same weight efficiencies, the rate of nickel deposition is larger in the acid solution.

2. Cobalt

(a) Alkaline Solutions

Some investigators [2 3], by using highly concentrated solutions of hypophosphite, obtained cobalt in flake and powdered form by a reduction similar to that described for nickel. In the studies by Scholder and Heckel [3], cobalt powder was obtained from a strongly alkaline tartrate solution. The black powder contained 90 to 92 percent of cobalt and 4 to 6 percent of phosphorus. The solution slowly decomposed upon standing at room temperature and the reaction became vigorous upon heating.

[2] Paal and Friedrici, Ger. deut. chem. Ges. **64**, 2561 (1931).
[3] Sholder and Heckel, Z. anorg. allgem. Chem. **198**, 329 (1931).

In the present studies, it was found that by reducing the concentration of the solution considerably, the formation of the powder was prevented, and smooth, adherent deposits of cobalt were formed on metal surfaces immersed in the hot solution. The alkaline-cobalt solution is very similar to the alkaline-nickel solution in composition and operation. It is composed of soluble salts of cobalt, hydroxycarboxylates, ammonia, and hypophosphite. The hydroxycarboxylic salts are used to prevent the precipitation of cobalt in the alkaline solution, and to afford deposits of good physical properties. The most suitable hydroxycarboxylic salts are the tartrate and citrate. Other salts, such as sodium hydroxyacetate, gluconate, and salicylate are unsatisfactory because they slow down the production of deposits. Deposits produced in the citrate solutions have better physical properties than those from the tartrate solutions, which tend to be more dull, powdered, and porous.

In the cobalt solution, ammonium salts decrease the rate of deposition to a considerable extent, in contrast to their effect in the alkaline nickel solution. However, this decrease in rate is compensated for by the fact that the deposits are superior in physical properties to the dull, rough, and porous deposits formed at exceedingly high rates in the solutions free from ammonium salts. The optimum concentration of ammonium salts is between 25 and 50 g/liter; an excessive amount, for example 100 g/liter, decreases the rate of deposition to a negligible value.

The cobalt concentration should be between 2 and 10 g/liter. A concentration much above this causes darkening of the deposits and finally reduces the rate of deposition.

The sodium hypophosphite is used in higher concentrations in the cobalt than in the nickel solutions. Very little cobalt reduction occurs with sodium hypophosphite equal to 10 g/liter, but the rate of deposition is steadily increased as the hypophosphite concentration is increased to 100 g/liter. For optimum efficiency, it is recommended that the sodium hypophosphite content be 20 g/liter.

For most purposes, ammonium hydroxide is used to regulate the pH of the solution. Other hydroxides can be used, but, when this is done, more care is required in making additions in order to keep within the pH range.

Table 6 shows the composition of some typ baths. Bath IV produces deposits of super physical properties. However, deposition may slow to start, and in such cases, it can be initiat in bath II before the parts to be plated are i mersed in bath IV.

TABLE 6. *Compositions of some of the alkaline-co solutions*

	Bath			
	I	II	III	IV
Cobalt chloride:	*g/liter*	*g/liter*	*g/liter*	*g/li*
$CoCl_2.6H_2O$	30	30	30	
Sodium hypophosphite:				
$NaH_2PO_2.H_2O$	20	20	20	
Rochelle salt:				
$NaKC_4H_4O_6.4H_2O$	200			
Sodium citrate:				
$Na_3C_6H_5O_7.5½\ H_2O$		35	100	
Ammonium chloride:				
NH_4Cl	50	50	50	
Rate of deposition:				
Millimeters per hour	0.0076	0.016	0.007	0.0
Inches per hour	.0003	.0006	.00027	.0
Appearance of deposit	Dull	Dull	Dull	Da
Alkali for neutralizing bath	NH_4OH	NH_4OH	NH_4OH	NH_4
pH	9 to 10	9 to 10	9 to 10	9 to

The pH of the solutions has a considerab effect upon the rate of deposition. For best re sults, the pH should be kept above 9 for the cobal whereas, a pH of 8 to 9 was satisfactory for th alkaline nickel solutions. The yield or efficienc of the deposition of cobalt, based on the decom position of hypophosphite, is 66 percent when relatively large surface is coated in a small volum of solution. When the area of metal surface in given volume of solution is decreased, the efficienc is lowered.

(b) Acid Solutions

The reduction of cobalt from acid baths is no satisfactory. A very thin film of cobalt forms o copper and steel in solutions of certain compos tions, but the deposit does not build up and cove irregularly. From experiments in which the com position, concentration, metal surfaces, and pr treatments were varied widely, it was conclude that deposition from acid solutions is impractica

3. Solutions for Depositing Nickel-Cobalt Alloy

A deposit of a nickel-cobalt alloy can be ob tained by using an alkaline solution containing soluble salts of both metals. In a solution con

ining equal parts of nickel and cobalt, the resulting deposit contains about 65 percent of ckel. When the metal ratio, Co/Ni, in the solution is changed to 2, the resulting deposit contains about 50 percent of each metal.

The conditions for plating, with respect to pH, mperature, and composition, are the same as r alkaline electroless plating of nickel or cobalt. he pH should be 8 or above, and the temperature least 90°C. A typical alloy bath contains:

	g/liter
Cobalt chloride	30
Nickel chloride	30
Sodium citrate	100
Ammonium chloride	50
Sodium hypophosphite	20
Ammonium hydroxide to regulate pH.	

his solution deposits a semibright cobalt-nickel loy at the rate of nearly 0.0006 in. (0.015 mm) in 1 hour. Changes in the composition of the solution cause changes in the rate of deposition and in the physical properties of the deposit that are similar to those mentioned for the individual metals. When sodium citrate (100 g/liter) is used in place of Rochelle salts, the deposits are brighter and smoother, but the corrosion resistance is inferior.

In the acid solution, an alloy cannot be obtained, as nickel alone is deposited. Only 0.25 percent of cobalt was found in a deposit from an acid solution containing equal amounts of each metal.

III. Effects of Impurities

Certain metals and radicals in the plating solutions decrease the rate of metal reduction. Table 7 shows the concentrations at which some metals will inhibit plating.

TABLE 7. *Effect of impurities*

Impurity	Alkaline-nickel bath		Acid-nickel bath		Alkaline-cobalt bath	
	Impurity	Effects	Impurity	Effects	Impurity	Effects
	g/liter		g/liter		g/liter	
SO_4	0.01	Copper deposition	0.1	Rate decreased	0.1	Normal deposition.
Cl	1.0	Rate decreased	.1	Normal deposition	1.0	Rate decreased.
Cl	0.1	No deposition	.1	Rate decreased	0.1	Rate greatly decreased.
Cl	1.0	Normal deposition	.1	Normal deposition	1.0	Rate decreased.
Cl	1.0	do	.1	do	1.0	Normal deposition.
Cl	1.0	do	.1	do	1.0	Rate decreased.
SCN	0.01	No deposition	.1	No deposition	0.01	No deposition.
Cl	.1	do	.1	do		
CN	.01	do	.01	Normal deposition	.01	No deposition.
H_2PO_2	10	Rate decreased			10	Rate decreased.

The cobalt solution is the most sensitive, and he acid-nickel solution the least sensitive to mpurities. Palladium does not inhibit the deposition, but it causes a gradual decomposition of he hypophosphite when present in the solution.

To render the contaminated solutions operable gain, the impurities must be removed. The emoval can be made by conventional means of eparation. For example, the suggested manner or removing cadmium from the solution is to djust the bath to pH 3.5 to 4.0 and to pass ydrogen sulfide through the solution for about 5 minutes. The cadmium is precipitated under hese conditions and it can be separated by filtering. If the pH of the solution is above 4, much ickel is precipitated, and if the pH is below 3, he cadmium precipitation is not complete.

Frequently, failure to plate is caused by poisoning of the metal surface. An interesting example of this is the passivation of a gold surface by cyanide solutions. Massive palladium does not always have the catalytic properties shown by the freshly prepared palladium film.

IV. Deposition on Various Surfaces

Iron, nickel, gold, cobalt, aluminum, and palladium have catalytic properties that initiate the reduction of the nickel and cobalt immediately upon their introduction into the hot solution. Zinc surfaces reduce some nickel, but the deposits have very poor physical properties. Some metals, particularly silver, occasionally act as catalytic surfaces.

Deposition can be obtained on noncatalytic metal surfaces such as platinum, copper, and brass, if certain measures are taken prior to immersing the metal into the plating solution. Lead and cadmium are noncatalytic metals that are not favorably affected by pretreatments, and deposition cannot be induced upon their surfaces. To induce deposition on specific noncatalytic surfaces and on certain catalytic surfaces that may be temporarily passivated, three methods may be used: (1) Change the composition of the plating solution (applicable to alkaline solutions only), (2) make contact with a more electronegative metal, and (3) deposit a thin layer of a catalytic metal on the surface of the noncatalytic metal. The latter two processes are applicable to both alkaline and acid solutions.

Procedure (1). Copper and brass can be plated in alkaline solutions containing no ammonium salts, but these solutions are not as stable as the ammoniacal solutions that have been recommended previously. As much as 0.0001 in. (0.0025 mm) of nickel is deposited on copper in 30 minutes from solutions containing:

	g/liter
Nickel chloride	30
Sodium hypophosphite	20
Rochelle salt	200
Sodium hydroxide to regulate pH to 8 to 10.	

Because of the instability of this solution, this procedure is not of practical value. If an excess of sodium or potassium hydroxide is used in regulating the pH, metal compounds will precipitate, and in turn, may act as nuclei for vigorous reduction of the metal and thus cause rapid decomposition of the solution. It is of interest that, although metal reduction is induced on copper surfaces in this type of solution, it does not consistently occur on steel surfaces. This is opposite to the behavior of these metals in the ammoniacal solutions.

(2). It was learned in this research that some noncatalytic metals can be plated by momentarily bringing a more electronegative metal, such as aluminum or iron into contact with the surface of the article while it is immersed in the electroless solution.[4] The contact needs to be of only short duration to initiate the deposition on the noncatalytic surface. Once the plating is started, presumably as a result of galvanic action, the reduction continues on the nickel that is first deposited. By this procedure, such metals as silver, copper, and brass can be activated so as to cause deposition of nickel upon their surfaces. Lead cannot be so plated. See table 8.

TABLE 8. *Pretreatments for noncatalytic surfaces*

+, surface will plate; −, surface will not plate

Metal surface	Contact process			Palladium dip		
	Alkaline Ni	Acid Ni	Alkaline Co.	Alkaline Ni	Acid Ni	Alkaline [illegible]
Copper	+	+	+	+	+	+
Brass	+	+	+	+	+	+
Platinum	+	+	+	−	−	−
Gold [a]	+	+	+	+	+	+
Silver	+	+	+		−	−
Lead	−		−	−	−	−

[a] Although gold is listed as catalytic for this process, it is frequently [illegible] tive.

(3). The third method of initiating deposition involves depositing minute amounts of catalytically active metals, such as palladium or rhodium, upon the noncatalytic surface. This can be done by dipping the metal into a solution containing palladium, 0.02 g/liter, and HCl (20 ml/liter). This dip is made after the conventional cleaning and immediately prior to immersion in the hot nickel solution. The immersion deposit of palladium is visible as a faint tarnishing, and is sufficient to catalyze the nickel reduction. This procedure is particularly satisfactory for obtaining deposits of nickel on copper and copper base alloys. The time required for immersion is dependent upon the cleaning treatment that the metal is given prior to the palladium dip, and also upon the temperature of the palladium solution.

Though not always necessary, a preliminary bright dip (in H_2SO_4 and HNO_3 or H_3PO_4 and HNO_3) is recommended for copper and brass surfaces. If copper is given a bright dip, the time required for immersion in the palladium solution at 25° C is only a few seconds; otherwise the immersion in the palladium solution should be increased to several minutes. With or without a bright dip, brass should be immersed in a palladium solution at 60° C for about 1 minute.

In spite of palladium being a precious metal

[4] William Paecht of the Wright Aeronautical Corp., in a subsequent communication to the authors, suggested the use of iron or steel for this purpose. A copy of a note was recently received that was published in Science and Culture (Calcutta), **12**, 503 No. 10 (April 1947), by A. P. Goswami. He also reported successful deposition of nickel on copper, brass, and platinum by bringing them into contact with steel.

s treatment is relatively inexpensive, because the very small amount of palladium consumed the process. At the current price of palladium bout $1 per g), the solution will not cost more an about $0.02 per liter. Only very thin films palladium are required; in fact the film used is most of unimolecular thickness, (about 2×10^{-8} n or 8×10^{-9} in.) as judged by the palladium nsumption. One liter of solution, containing 01 g of palladium, is sufficient to treat nearly 200 m^2 (20 ft.^{2}) of metal surface.

Plastic surfaces are noncatalytic, and none of the above procedures will initiate the nickel eposition. In an endeavor to plate plastics, everal types were tried in the hot nickel solution. Even when precleaned with organic solvents and cids, the plastics remained noncatalytic. No eposition occurred on the surface when immersed highly concentrated solutions. When a plastic as silvered prior to immersing in the nickel solu-on, satisfactory deposition failed to occur. his failure was due primarily to the silver flaking rom the plastic in the hot solution. Other ethods of applying a metal film to the plastic ight be more successful.

V. Mechanism of the Reaction

The data given in section II regarding the effect f concentration of the bath constituents on the ate of reaction show that the reaction does not o according to the equations. If the reaction roceeded in the fashion expressed in eq 1, the ate of deposition of nickel would be proportional o the concentration of hypophosphite and nickel. s previously discussed, the rate of deposition in he acid solution is virtually unaffected by the oncentration of the reactants, and in the alkaline olution is affected only by the concentration of he hypophosphite and not by that of the nickel. herefore, the reaction does not follow a simple ourse, but undergoes intermediate steps.

Actually, the rate of the reaction is affected as uch by the change in pH and the concentration nd specific nature of the organic salts as by the oncentration of the primary reactants. We have ttempted to explain the reaction by one of two ypothesis, neither of which is applicable to all the henomena.

One suggested mechanism is that the reaction hat determines the rate is the reaction of hypophosphite (eq 2) to produce hydrogen which, in turn, reduces the nickel on the catalytic surface. There is some evidence to support this mechanism for the alkaline solutions. Hydrogen evolution occurs at the surface of catalytic metals, even in the absence of nickel or cobalt salts, when immersed in the hot alkaline hypophosphite solutions. Furthermore, the potential of the catalytic metal in this solution is the same as the potential of the metal during the electroless plating process. The potential is -1.1 to -1.2 v, relative to the saturated calomel electrode (see table 9). This potential is more negative than the reversible potential of either hydrogen or nickel, and hence is sufficient to account for the separation of the free elements.

TABLE 9. *Electrode potentials (against saturated calomel electrode) in an ammoniacal nickel solution*

Electrode	Potential with respect to saturated calomel electrode	
	Before plating	After plating
Steel		−1.16
Aluminum		−1.2
Platinum	−0.44	[a] −1.2
Copper	−.60	[a] −1.25
Silver	−.17	[a] −1.15
Gold	−.04	[a] −1.23

[a] Plating induced by contact with aluminum.

This explanation does not apply to the reaction in the acid solution in which, as already emphasized, the rate of deposition is not affected by the concentration of the hypophosphite. Furthermore, the catalytic decomposition of hypophosphite with the production of hydrogen does not occur at metallic surfaces in the absence of nickel salts. The fact that the rate of deposition of nickel is increased considerably by the movement of the metal being plated would seem to indicate that the rate may be controlled by some type of diffusion process. Agitation of the metal does not affect the rate in the ammoniacal solution. Therefore, the mechanism seems to be different for acid and alkaline solutions.

Another possible mechanism for electroless plating is that the presence of hydrogen on the catalytic metal constitutes a galvanic cell, in which hydrogen is the anode and the metal the cathode. The process could then be considered as electrolytic. The potential of the metal during the

electroless process is negative enough for such to be the case in both the acid and alkaline solutions. (See table 10.) An objection to this mechanism is that from an acidic electroless solution containing equal amounts of cobalt and nickel, only nickel is deposited. If this were an electrolytic process, more cobalt would be deposited than nickel.

TABLE 10. *Summary of potentials (against saturated calomel electrode) in solutions containing hypophosphite*

Solutions		Condition of electrode	Average potential
No.	Composition		
A	Alkaline nickel with ammonium salts.	During deposition	−1.2
B	Alkaline nickel with no ammonium salts.	do	−1.3
C	Same as B, but without nickel	As hydrogen evolution occurs	−1.3
D	Alkaline cobalt with ammonium salts.	During deposition	−1.2
E	Acid nickel with hypophosphite and organic salt.	do	−0.9
F	Same as E, but without nickel	No observable reaction at catalytic surfaces	−.8
G	Same as E, but without hypophosphite.	During electrolysis at 0.5 amp/dm²	−.77
H	do	Theoretical H_2 potential	.59

In connection with the measurement of the potentials of electroless plating, it was of interest to determine the effect of impurities on the potentials. As small concentrations of cadmium inhibit deposition, this impurity was selected for study. The addition of cadmium to the extent of 100 mg/liter in the course of an electroless plating experiment caused the potential of the work to become more noble, as shown in the following data, and both the metallic deposition and hydrogen evolution ceased. (Potentials measured against calomel half-cell.)

	Volt
Potential of steel before hypophosphite is added to the bath	−1.15
Potential of surface while plating with hypophosphite added to the bath	−1.28
Potential of surface after cadmium chloride, 0.01 g/liter is added to bath	−1.14

VI. Adhesion of Deposits

The adhesion of the deposits to the base metal is such that the deposits will not flake off, but in some cases will detach on flexing. The adhesion to various metals can be improved by variations in the cleaning of the metal prior to immersion in the reducing solution. Excellent adhesion to steel can be obtained by an anodic treatment of the steel in a 70-percent sulfuric acid, but in order to make the process independent of current, it is preferable to use a dip in concentrated (95%) sulfuric acid.

The adhesion to surfaces that have been given a palladium dip may be inferior because of the usually poor adhesion of immersion coatings of palladium to the base metal. The adhesion of the nickel to aluminum surfaces is unsatisfactory, but can be improved if the aluminum is given a zincate dip prior to immersion in the reducing solution.

VII. Physical Properties of the Deposits

1. Microstructure

As shown by figures 1, 2, and 3, the deposits have laminations running parallel to the base metal, and within each layer there is a columnar structure perpendicular to the base metal. Figures 2 and 3 show that upon heating, precipitation occurs.

2. Hardness

The hardness of the electroless nickel deposits is greater than that of electrodeposited nickel. The Knoop hardness number for nickel, electrodeposited in a Watts type bath, may vary from 120 to 450. For the electroless nickel from the alkaline citrate solution, the hardness is about 425, and from the ammoniacal solution containing no organic salts, about 530. Deposits from the acid-nickel solution have an average hardness of about 500. Upon heating the electroless nickel deposits, their hardness is increased; this is in contrast to the so-called "hard" nickel that is usually electrodeposited from a bath containing ammonium salts and has an initial hardness of about 500, but which softens upon heating. A possible explanation of this difference may be the occurrence of precipitation hardening in the electroless deposits. As formed, the electroless deposits are brittle, but they become ductile upon heating.

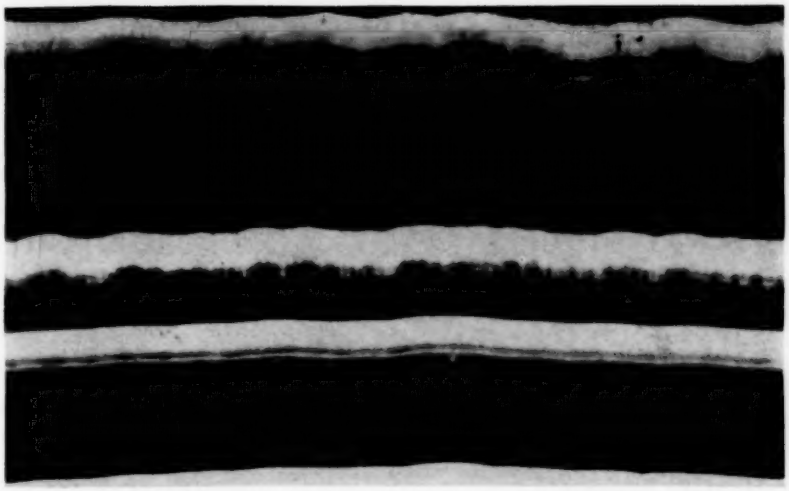

FIGURE 1. *Electroless nickel deposit from an acid solution showing laminations and columnar structure,* ×500.
Knoop hardness number 500.

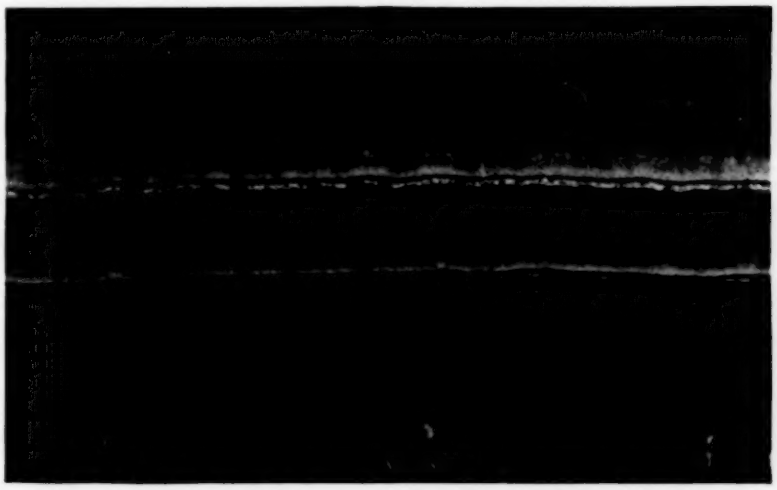

FIGURE 2. *Electroless nickel deposit, after annealing at 400° C for ½ hr,* ×500.
Knoop hardness number 800.

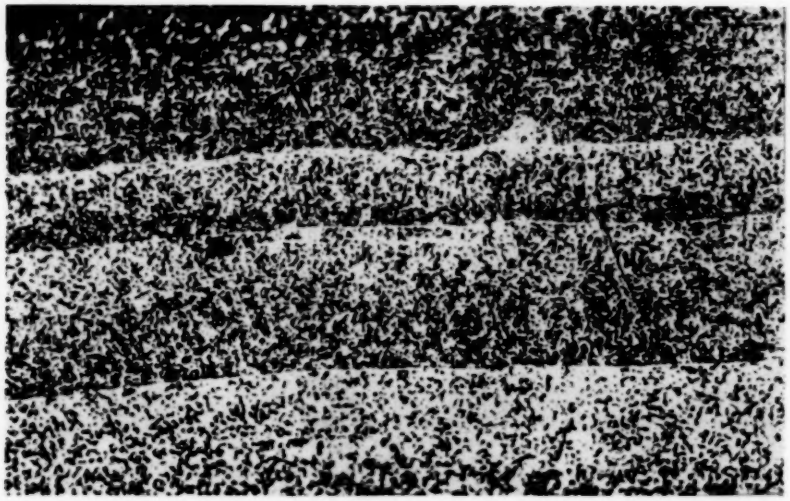

FIGURE 3. *Electroless nickel deposit, after annealing at 800° C for ½ hr, showing apparent precipitation,* ×500.
Knoop hardness number 470.

3. Magnetic Properties

Qualitative measurements of magnetic properties were made by measuring the attractive force of a permanent magnet for the coating. It was found that the electroless nickel is not as magnetic as electrodeposits from the Watts nickel bath. The magnetic properties of electroless nickel are increased by annealing at 400° C for about 30 minutes.

4. Appearance

In general, the alkaline nickel solutions produce the brightest deposits. Deposits from the acid-nickel solutions can be brightened somewhat by the addition of cobalt or very small amounts of cadmium (0.01 g/liter), but by such additions, the rate of deposition is decreased. The cobalt deposits are dull (similar to electroplated cobalt in appearance) and tend to be dark when deposited at high rates.

5. Corrosion Resistance

In the 20-percent salt-spray test, electroless nickel, deposited on steel from either the acid or alkaline solutions, affords protection to the steel equal to that of electroplated nickel. The cobalt deposits from the citrate solutions give protection to steel superior to those from the tartrate solutions, but neither are comparable to electroplated deposits of the same thickness. The electroless deposits of Co-Ni alloy fail in the salt spray sooner than the single deposits of cobalt or nickel.

6. Composition

Nickel deposits from the alkaline solutions contain an average of 93.5 percent of nickel and from the acid solutions, an average of 93.1 percent of nickel. The electroless cobalt deposits contain 94.5 percent of cobalt. Although quantitative analysis has not been made, qualitative tests indicate that the deposits contain considerable amounts of phosphides.

7. Reaction with Ferric Chloride

By immersing electroless nickel deposits in an acid solution of ferric chloride, 200 g/liter, the metallic surface is blackened. It has not been possible to produce a uniform degree of blackening, and hence this property has little commercial value. The electroless black nickel does not protect steel in the 20-percent salt spray tests as well as does electroplated black nickel of the same thickness.

VIII. Possible Analytical Applications

1. Detection of Palladium

As previously described, reduction in the hypophosphite solutions can be initiated by the presence of small amounts of palladium. Feigl

nd Frankel [5] used this reaction to detect palladium. They added the unknown to a hot solution containing nickel and hyposphite and observed the formation of a powder or mirror of nickel on the wall of the test tube. They were able to detect one part of palladium in a billion parts of solution.

As a result of our work, an alternative procedure is suggested as being more direct. A cleaned copper wire is immersed in an acidified solution to be tested; any palladium present will tend to be reduced on the copper surface. Nickel will then reduce on the wire upon introducing the latter into the typical electroless hypophosphite solution (composition suggested in section II, 1, (a). This is not a specific test, as rhodium will also cause copper to react in a similar manner.

[5] Ber. deut. chem. Ges. **65**, [B], 539 (1932).

2. Quantitative Reduction of Nickel

Paal and Freiderici [6] reduced nickel compounds to the metal in an ammoniacal hypophosphite and tartrate solution. They were not able to obtain complete precipitation of the metal by this method.

In the present studies, a quantitative reduction of nickel was obtained by increasing the concentration of the sodium hypophosphite to 50 g/liter and that of ammonium chloride to about 600 g/liter. The reaction occurred spontaneously without a catalyst being present. The nickel powder was separated by filtration, leaving the filtrate free from nickel as indicated by a test with dimethylglyoxime. The utility of this separation has not been investigated.

WASHINGTON, July 18, 1947.

[6] Ber. deut. chem. Ges. **64**, 1766 to 1776 (1931).

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Calculations on Countercurrent Electromigration [1]

By G. Breit [2] and F. L. Friedman

The mathematical problems presented by the countercurrent electrolysis method for isotope separation are treated under the simplified assumptions described in the text as (a), (b), (c), (d), (e), and (f) in section II, 2, of this paper. The solutions are worked out in section II, 3, for a tube of finite length. The formulas are put into numerical form in equations 9e, 9f, etc. Simpler formulas are obtained in section II, 4, in the approximation of tubes of infinite length. Some of the results are presented in the form of graphs that are described in section III. The orders of magnitude of effects to be expected are discussed in section IV.

I. Introduction

The countercurrent electromigration method has been found to give isotope separation in the case of potassium [1, 2] [3] and chlorine [3]. In the present report some diffusion problems of this method are treated mathematically. Formulas are given for the calculation of the concentration along the tube. Some typical numerical examples are given to illustrate the use of the formulas and graphs and to show the variation of concentration with time and distance.

II. Calculations

1. Notation

n_l = number of more mobile ions per cubic centimeter (supposedly light).

n_h = number of less mobile ions per cubic centimeter (supposedly heavy).

μ_l, μ_h = mobilities of light and heavy ions respectively.

D_l, D_h = effective diffusion coefficients of light and heavy ions.

v = velocity of liquid flow (positive when toward cathode).

E = electric field (positive when directed from anode to cathode).

n_l°, n_h° = normal values of n_l, n_h.

μ = common symbol for μ_l or μ_h if distinguishing between them is immaterial.

D = common symbol for D_l or D_h if distinguishing between them is immaterial.

x = distance along tube measured from anode to cathode.

V = volume of cathode compartment.

A = cross sectional area of tube free to carry electric current.

$\Delta\mu = \mu_l - \mu_h$.

L = length of tube.

t = time counted from beginning of experiment.

$L' = V/A$ = effective length of cathode.

2. Simplifying Assumptions and Basic Equations

It is assumed that: (a) The mobilities and the diffusion coefficients have the same values throughout the tube. This is not true, but it is felt that the variation of these quantities may be neglected for the present preliminary estimates. (b) The electric field is assumed to be constant along the tube. This is also not strictly true. As the electric field could be maintained at a constant value, this assumption should not matter much. (c) The cathode is assumed to be stirred perfectly. (d) The concentrations in the anode are supposed to be maintained at their normal

[1] This paper will appear in volume 6, division III, of the Manhattan Project Technical Series.

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[3] Figures in brackets indicate the literature references at the end of this paper.

values. (e) The solution is supposed to be completely dissociated. (f) Forces acting on ions due to space charge effects are neglected.

At a point in the tube having distance, x, from the anode the flux of light ions is

$$\phi_l=(\mu_l E+v)n_l-D_l\frac{\partial n_l}{\partial x} \tag{1}$$

The first term takes account of the combined action of the electric field which gives rise to the migration and of the counter current velocity, v. One has, therefore,

$$\frac{\partial n_l}{\partial t}+\frac{\partial}{\partial x}\left[n_l(\mu_l E+v)-D_l\frac{\partial n_l}{\partial x}\right]=0 \tag{2}$$

$$\frac{\partial n_h}{\partial t}+\frac{\partial}{\partial x}\left[n_h(\mu_h E+v)-D_h\frac{\partial n_h}{\partial x}\right]=0 \tag{2a}$$

for the equations expressing equilibrium of the light and heavy ions within the tube. At the cathode compartment $x=L$. Since the liquid inside the cathode is stirred one has

$$\frac{V}{A}\frac{\partial n_l}{\partial t}=\phi_l=(\mu_l E+v)n_l-D_l\frac{\partial n_l}{\partial x}\ (x=L) \tag{2b}$$

$$\frac{V}{A}\frac{\partial n_h}{\partial t}=\phi_h=(\mu_h E+v)n_h-D_h\frac{\partial n_h}{\partial x}\ (x=L) \tag{2c}$$

It is convenient to introduce

$$a_l=\mu_l E+v,\ a_h=\mu_h E+v \tag{2d}$$

$$\tau_l=\frac{a_l^2}{D_l}t,\ \tau_h=\frac{a_h^2}{D_h}t \tag{2e}$$

$$\xi_l=\frac{a_l}{D_l}x,\ \xi_h=\frac{a_h}{D_h}x \tag{2f}$$

$$\lambda_l=\frac{a_l}{D_l}L,\ \lambda_h=\frac{a_h}{D_h}L \tag{2g}$$

$$\gamma_l=\frac{V}{A}\frac{a_l}{D_l}=\frac{V}{AL}\lambda_l=\frac{L'}{L}\lambda_l;\ \gamma_h=\frac{L'}{L}\lambda_h \tag{2h}$$

This amounts to introducing units that are somewhat more natural for the discussion than the original units. In terms of the natural units one has instead of eq 2 and 2a;

$$\frac{\partial n_l}{\partial \tau_l}=\frac{\partial^2 n_l}{\partial \xi_l^2}-\frac{\partial n_l}{\partial \xi_l},\ \frac{\partial n_h}{\partial \tau_h}=\frac{\partial^2 n_h}{\partial \xi_h^2}-\frac{\partial n_h}{\partial \xi_h} \tag{3}$$

The conditions for the cathode compartment become

$$\left(\gamma_l\frac{\partial n_l}{\partial \tau_l}\right)_{\lambda_l}=\left(n_l-\frac{\partial n_l}{\partial \xi_l}\right)_{\lambda_l},\ \left(\gamma_h\frac{\partial n_h}{\partial \tau_h}\right)_{\lambda_h}=\left(n_h-\frac{\partial n_h}{\partial \xi_h}\right)_{\lambda_h} \tag{3a}$$

The problem is defined by equations 3, 3a, and the conditions

$$n_l(o,t)=n_l^\circ,\ n_h(o,t)=n_h^\circ \tag{3b}$$

$$n_l(x,o)=n_l^\circ,\ n_h(x,o)=n_h^\circ \tag{3c}$$

which express the fact that at all times the concentrations are normal at the anode and also that at $t=0$ the concentrations are normal throughout the tube.

Since the equations are of the same form for n_l and n_h, the indices l and h may be dropped in most of the work.

3. Tube of Finite Length

In this section an exact solution for a tube of finite length is given. The motion of one isotope only is considered and the formulas are supposed to be applied by working out separately the concentrations of the two isotopes. The indices l, h are omitted in the discussion of the behaviour of a single isotope. The equation

$$\frac{\partial n}{\partial \tau}=-\frac{\partial n}{\partial \xi}+\frac{\partial^2 n}{\partial \xi^2} \tag{4}$$

is being solved subject to boundary conditions (eq 3a, 3b, and 3c).

For $\tau=\infty$ one has in addition

$$n(\xi,\ \infty)=n^\circ e^{\xi}. \tag{4a}$$

The solution can be constructed by expanding the initial state in terms of a complete set of functions. For $\gamma=0$ the functions are mutually orthogonal and the method is then well known. For $\gamma\neq 0$ the functions are not mutually orthogonal. It is nevertheless possible to give an explicit usable solution in this case also.

Equation 4 is first transformed by

$$n=e^{t/2}N \tag{4b}$$

It assumes the form

$$\frac{\partial^2 N}{\partial \xi^2}-\frac{N}{4}=\frac{\partial N}{\partial \tau} \tag{4c}$$

The function n is expanded as

$$n(\xi,\tau)=n^\circ e^{\xi}+e^{\xi/2}\sum a_i v_i(\xi)e^{-\beta_i\tau} \tag{4d}$$

where $v_i(\xi)e^{-\beta_i\tau}$ are solutions of eq 4c so that

$$\frac{d^2v_i}{d\xi^2}+\left(\beta_i-\frac{1}{4}\right)v_i=0. \tag{4e}$$

The functions v_i are taken so as to satisfy the boundary conditions

$$v_i(0)=0,\left[\frac{dv_i}{d\xi}\right]_{\xi=\lambda}=\left(\beta_i\gamma+\frac{1}{2}\right)v_i(\lambda) \tag{4f}$$

The first of these corresponds to eq 3b, the second to eq 3a. The condition in eq 3c is taken care of by making

$$2n^\circ\sinh\frac{\xi}{2}+\sum a_i v_i(\xi)=0 \tag{4g}$$

All initial conditions are satisfied automatically as a result of eq 4f and 4g. It remains to determine the a_i.

Combining two previous equations one has

$$v_j(\lambda)v_i'(\lambda)-v_i'(\lambda)v_i(\lambda)=(\beta_j-\beta_i)\int_0^\lambda v_j(\xi)v_i(\xi)d\xi$$

Eliminating v_i', v_j' by means of eq 4f, one has for $i\neq j$

$$\int v_i(\xi)v_j(\xi)d\xi+\gamma v_i(\lambda)v_j(\lambda)=0. \tag{5}$$

In order to expand the function

$$-2n^\circ\sinh(\xi/2)=f(\xi)=\Sigma a_i v_i(\xi) \tag{5a}$$

the functions $v_i(\xi)$ are first normalized to unity:

$$\int_0^\lambda v_i^2(\xi)d\xi=1 \tag{5b}$$

By integration one obtains from eq 5a,

$$a_i-\gamma\sum_{i\neq j}v_i(\lambda)v_j(\lambda)a_j=f_i,\ f_i=\int_0^\lambda v_i(\xi)f(\xi)d\xi \tag{5c}$$

The abbreviations

$$v_i=v_i(\lambda),\ \sigma=\Sigma a_j v_j=f(\lambda) \tag{5d}$$

are introduced. In terms of these, eq 5c gives

$$a_i=\frac{f_i+\gamma v_i\sigma}{1+\gamma v_i^2} \tag{5e}$$

The boundary conditions in eq 4f and the normalization in eq 5b are satisfied by

$$v_0(\xi)=\frac{\sqrt{2/\lambda}\sinh(r\xi/2)}{\sqrt{\sinh r\lambda/r\lambda-1}};\ r=\sqrt{1-4\beta},\ r=\text{real number} \tag{6}$$

where

$$\tanh\frac{r\lambda}{2}=\frac{r}{1+\gamma(1-r^2)/2} \tag{6a}$$

determines r.

Equation 4c is similar in form to the time dependent wave equation in wave mechanics. Only real $\beta\geqq 0$ need be considered, therefore. Accordingly, only real or pure imaginary values of r are of interest.

For $\gamma\geqq 0$, $\lambda>0$ eq 6a has in addition to $r=0$ at most one real root for r and this lies in $0<r<1$. In addition there are pure imaginary roots

$$r=i\rho_s \tag{6b}$$

These satisfy

$$\tan\left(\frac{\rho_s\lambda}{2}\right)=\frac{\rho_s}{1+\gamma(1+\rho_s^2)/2} \tag{6c}$$

There is an infinite number of roots ρ_s forming a discrete set.

If the velocity of the liquid is higher than the migration velocity then λ and γ have negative values. From eq 6a one obtains

$$\lambda=\frac{1}{r}ln\left[\frac{1+r}{1-r}\frac{1+\gamma(1-r)/2}{1+\gamma(1+r)/2}\right] \tag{6d}$$

For $\gamma<-2$, values of r in $0<r<1+2/\gamma$ give values of λ in $-\frac{4/|\gamma|}{1-2/|\gamma|}>\lambda>-\infty$. For $\gamma>-2$ there are no real roots for r. For $a<0$ there is thus also at most one real root for r.

Performing the calculation according to eq 4d, 5a, 5e, and making use of eq 6a and 6c, it is found that

$$n(\xi,\tau)=n^\circ e^{\xi}-\frac{8}{\lambda}n^\circ e^{\frac{\xi-\lambda}{2}}\sum_{s=0}^{\infty}\frac{\sinh\frac{r_s\lambda}{2}\sinh\frac{r_s\xi}{2}e^{-\frac{1}{4}(1-r_s^2)\tau}}{\frac{2}{\lambda}-1+r_s^2+\frac{2}{\lambda}\frac{\left(\frac{\gamma}{2}\right)\left(1+\frac{\gamma}{2}\right)(r_s^2-1)}{\left(1+\frac{\gamma}{2}\right)-\frac{\gamma^2r_s^2}{4}}} \tag{7}$$

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where the summation covers real and imaginary r_s. For imaginary r_s eq. 6b and 6c are used and $\sinh(r_s\lambda/2)$ is replaced by $i\sin(\rho_s\lambda/2)$. As a special case

$$n(\lambda,\tau)=n^\circ e^\lambda-\frac{8}{\lambda}n^\circ\sum_{s=0}^{\infty}\frac{\frac{r_s^2}{1-r_s^2}e^{-\frac{1}{4}(1-r_s^2)\tau}}{\left(\frac{2}{\lambda}-1+r_s^2\right)\left[\left(1+\frac{\gamma}{2}\right)^2-\frac{\gamma^2}{4}r_s^2\right]-\frac{\gamma}{\lambda}\left(1+\frac{\gamma}{2}\right)(1-r_s^2)}$$

gives the concentration at the cathode. For large positive γ the real root moves toward unity so that $r_0=1-\epsilon$ where $\epsilon<<1$. In this limit one has approximately

$$\gamma=\frac{2/\epsilon}{e^\lambda-1} \tag{8}$$

The imaginary roots contribute terms in $1/\gamma^2$ and become small for $\gamma\to\infty$. Equation 7a gives in this limit

$$n(\lambda,\tau)=n^\circ e^\lambda-n^\circ(e^\lambda-1)e^{\frac{-\tau}{\gamma(e^\lambda-1)}} \tag{8a}$$

so that the approximate time constant in units D/a^2 is

$$\tau^\circ=\gamma(e^\lambda-1), \tag{8b}$$

which corresponds to a time constant in seconds

$$T^\circ=\frac{V}{Aa}(e^\lambda-1) \tag{8c}$$

If in addition $\lambda<<1$ then

$$T^\circ\cong\frac{VL}{AD}=\frac{L'L}{D} \tag{8d}$$

If $a<0$, eq 8 to 8d still hold for large values of $-\gamma$.

For a small cathode compartment, one has the simpler formulas:

$$n(\xi,\tau)=$$

$$n^\circ e^\xi-\frac{8n^\circ}{\lambda}e^{\frac{\xi-\lambda}{2}}\sum_{s=0}^{\infty}\frac{\sinh\frac{r_s\lambda}{2}\sinh\frac{r_s\xi}{2}e^{-\frac{1}{4}(1-r_s^2)\tau}}{-1+r_s^2+2/\lambda} \tag{9}$$

$$n(\lambda,\tau)=n^\circ e^\lambda-\frac{8}{\lambda}n^\circ\sum_{s=0}^{\infty}\frac{r_s^2e^{-(1-r_s^2)\tau/4}}{(1-r_s^2)(-1+r_s^2+2/\lambda)} \tag{9a}$$

For $\gamma=0$, $\lambda=2$, the real root is in the process of becoming imaginary, and the corresponding term in the above formulas needs special consideration becoming indeterminate. Making $\lambda=2+\epsilon$ with $\epsilon\to0$ it is found that:

$$n(\xi,\tau)=n^\circ e^\xi-$$

$$n^\circ e^{\frac{\xi-2}{2}}\left\{3\xi e^{-\beta_0\tau}+\sum_1^{\infty}\frac{\sin\rho_s\sin(\rho_s\xi/2)e^{-\beta_s\tau}}{(\rho_s/2)^2}\right\} \tag{9b}$$

$$n(\lambda,\tau)=n^\circ e^2-n^\circ\left\{6e^{-\beta_0\tau}+\sum_1^{\infty}\frac{4}{1+\rho_s^2}e^{-\beta_s\tau}\right\} \tag{9c}$$

In this case the roots are known and are tabulated in Jahncke-Emde [4]. Substitution of numbers gives

$$\begin{aligned}n(\lambda,\tau)/n^\circ=e^2&-6e^{-\beta_0\tau}-0.18876e^{-\beta_1\tau}-\\&0.06592e^{-\beta_2\tau}-0.03336e^{-\beta_3\tau}-0.02011e^{-\beta_4\tau}-\\&0.01344e^{-\beta_5\tau}-0.00962e^{-\beta_6\tau}-0.00722e^{-\beta_7\tau}-\\&0.00562e^{-\beta_8\tau}-0.004496e^{-\beta_9\tau}-0.00368e^{-\beta_{10}\tau}-\\&0.00307e^{-\beta_{11}\tau}-0.002595e^{-\beta_{12}\tau}-0.00223e^{-\beta_{13}\tau}-\\&0.001929e^{-\beta_{14}\tau}-0.001688e^{-\beta_{15}\tau}-0.001489e^{-\beta_{16}\tau}-\\&0.001324e^{-\beta_{17}\tau}-0.001184e^{-\beta_{18}\tau}-0.001066e^{-\beta_{19}\tau}-\\&0.000965e^{-\beta_{20}\tau}-0.000877e^{-\beta_{21}\tau}-0.000801e^{-\beta_{22}\tau}-\ \ldots\end{aligned} \tag{9d}$$

Also

$$\begin{aligned}n(1,\tau)=n^\circ e-\frac{n^\circ}{\sqrt{e}}\{&3e^{-\beta_0\tau}-0.15087e^{-\beta_1\tau}-\\&0.04388e^{-\beta_2\tau}+0.02473e^{-\beta_3\tau}+\\&0.01374e^{-\beta_4\tau}-0.00979e^{-\beta_5\tau}-\\&0.00664e^{-\beta_6\tau}+0.00522e^{-\beta_7\tau}+\\&0.00390e^{-\beta_8\tau}-0.00323e^{-\beta_9\tau}-\ \ldots\}\end{aligned} \tag{9e}$$

The β's in eq 9d and in 9e are given by:

$$\beta_0=\frac{1}{4},\ \beta_1=\frac{1}{0.18876},\ \beta_2=\frac{1}{0.06592},\ \beta_3=\frac{1}{0.0335}$$

In order to see how the cathode volume affects the results, the above solution can be compared with that for $\lambda=2$, $\gamma=15.2195$. The choice of γ in this calculation is made so as to give $r_0=0.9$. Approximate values of the ρ's are $\rho_1=3.18$, $\rho_2=6.30$, $\rho_3=9.44$. For the cathode, one obtains by means of eq 7a,

$$\frac{n}{n^\circ}=7.3891-6.3885e^{-0.0099\tau}-$$

$$0.00043e^{-2.78\tau}-0.00004e^{-10.2\tau}-\ \ldots$$

which shows that in this case only the first term having the time constant $T=101D/a^2$ is of real importance. The approximation in eq 8b gives $T=97D/a^2$ and is suitable for an approximate estimate for this γ and λ. Because of the more rapid convergence of the series, calculations with large γ are easier than with small γ.

Another example of the application of eq 7a is $=2$, $r_0=0.90$, $\gamma=2.6995$ for which $\rho_1=3.331$, $=6.394$, and

$$\left(\frac{n}{n^\circ}\right)_{\xi=\lambda}=7.3891-6.376e^{-0.0475\tau}-0.01132e^{-3.025\tau}-$$
$$0.00115e^{-10.47\tau}-0.00025e^{-22.9\tau}-\ldots \quad (9f)$$

An example for negative a may also be given: $=-1, r_0=0.50, \gamma=-8.111, \rho_1=6.359, \rho_2=12.605$, which gives

$$\left(\frac{n}{n^\circ}\right)_{\xi=\lambda}=0.36788+0.6319e^{-\frac{3\tau}{16}}+$$
$$0.00028e^{-10.36\tau}+\ldots \quad (9g)$$

A consideration of these examples shows that for a rather large range of values of γ, the term in $e^{-\frac{1-r_0^2}{4}\tau}$ is the last important one. The relation $=\gamma(e^\lambda-1)$ for its time constant can be improved on by using a graphical or numerical solution of

$$\tanh\frac{r\lambda}{2}=\frac{r}{1+\gamma(1-r^2)/2}$$

and setting

$$\tau^\circ=\frac{4}{1-r_0^2} \quad (9h)$$

4. Tubes of Infinite Length

Substitution of different τ into eq 9d, 9e shows that the concentration at the cathode builds up much more rapidly than in the middle of the tube. For times appreciably smaller than the time constant the effect of the anode is, therefore, not important, and the calculation of exact solutions involves a needless amount of work. The initial stages of the building up of the concentration can be studied by supposing that the tube is infinitely long because the solution for an infinite tube gives practically zero concentration at the anode.

In discussing a tube of infinite length it is convenient to measure lengths from the cathode introducing

$$\eta=\lambda-\xi \quad (10)$$

The differential equation is

$$\frac{\partial^2 n}{\partial\eta^2}+\frac{\partial n}{\partial\eta}=\frac{\partial n}{\partial\tau}, \quad (10a)$$

and the boundary condition at the cathode is conveniently expressed in terms of

$$m=\frac{\partial n}{\partial\eta}+n \quad (10b)$$

for which

$$\left(\gamma\frac{\partial n}{\partial\tau}-m\right)_{\eta=0}=\left(\gamma\frac{\partial m}{\partial\eta}-m\right)_{\eta=0}=0 \quad (10c)$$

The quantity m is the flux density of ions divided by a. It has proved convenient to use m in constructing the solution because $m-\gamma\frac{\partial m}{\partial\eta}$ has the simple initial condition of being 1 throughout the length of the tube. It is thus possible to construct first the solution for $\gamma=0$, to equate the m obtained for $\gamma=0$ to $m-\gamma\frac{\partial m}{\partial\eta}$ and derive m for any γ. From m, one obtains n by quadratures.

For $a>0$, one finds

$$\frac{n-n^\circ}{n^\circ}=\frac{\sqrt{\tau/\pi}}{1+\gamma}e^{-\frac{(\eta+\tau)^2}{4\tau}}-\frac{1}{2}\left[1-\Phi\left(\frac{\eta+\tau}{2\sqrt{\tau}}\right)\right]+$$
$$\frac{e^{-\eta}}{2}\frac{\tau-\eta+\frac{1}{1+\gamma}}{1+\gamma}\left[1-\Phi\left(\frac{\eta-\tau}{2\sqrt{\tau}}\right)\right]+$$
$$\frac{(2+\gamma)\gamma}{2(1+\gamma)^2}e^{\frac{\eta+\tau}{\gamma}+\frac{\tau}{\gamma^2}}\left[1-\Phi\left(\frac{\eta+\tau}{2\sqrt{\tau}}+\frac{\sqrt{\tau}}{\gamma}\right)\right] \quad (11)$$

where

$$\Phi(x)=\frac{2}{\sqrt{\pi}}\int_0^x e^{-x^2}dx,\ \Phi(-x)=-\Phi(x). \quad (11a)$$

For $\eta=0$ i. e. for the cathode the above formula is somewhat shorter:

$$\left(\frac{n-n^\circ}{n^\circ}\right)_{\eta=0}=\frac{\tau+1+\gamma+\frac{1}{1+\gamma}}{2(1+\gamma)}\Phi\left(\sqrt{\frac{\tau}{2}}\right)+$$
$$\frac{(2+\gamma)\gamma}{2(1+\gamma)^2}e^{\frac{\tau}{\gamma}+\frac{\tau}{\gamma^2}}\left[1+\Phi\left(\frac{\sqrt{\tau}}{2}+\frac{\sqrt{\tau}}{\gamma}\right)\right]+$$
$$\frac{\sqrt{\tau/\pi}}{1+\gamma}e^{-\tau/4}+\frac{\tau}{2(1+\gamma)}-\frac{\gamma(\gamma+2)}{2(1+\gamma)^2} \quad (11b)$$

and for $\gamma=0$, the following simple form obtains:

$$\frac{n-n^\circ}{n^\circ}=\sqrt{\tau/\pi}e^{-\frac{(\eta+\tau)^2}{4\tau}}-\frac{1}{2}\left[1-\Phi\left(\frac{\eta+\tau}{2\sqrt{\tau}}\right)\right]+$$
$$\frac{e^{-\eta}}{2}(\tau-\eta+1)\left[1-\Phi\left(\frac{\eta-\tau}{2\sqrt{\tau}}\right)\right] \quad (11c)$$

The values of $\Phi(x)$ are available in Jahnke-Emde [4] in good detail and numerical calculation by means of eq. 11, 11b, and 11c is straightforward. A convenient form of m is

$$\frac{m}{n^\circ}=\frac{1}{2}+\frac{1}{\sqrt{\pi}}\int_0^{(\eta+\tau)/2\sqrt{\tau}}e^{-x^2}dx-\frac{e^{-\eta}}{\sqrt{\pi}(1+\gamma)}\int_{(\eta-\tau)/2\sqrt{\tau}}^{\infty}e^{-x^2}dx+\frac{2+\gamma}{\sqrt{\pi}(1+\gamma)}e^{(\eta+\tau)/\gamma+\tau/\gamma^2}\int_{(\eta+\tau)/2\sqrt{\tau}+\frac{\sqrt{\tau}}{\gamma}}^{\infty}e^{-x^2}dx. \quad (11d)$$

For $a<0$, λ, η, γ are negative and τ is positive. In place of eq 11, 11b, 11c, and 11d one has

$$\frac{n-n^\circ}{n^\circ}=-\frac{\sqrt{\tau/\pi}}{1+\gamma}e^{-(\eta+\tau)^2/4\tau}-\frac{1}{2}\left[1+\Phi\left(\frac{\eta+\tau}{2\sqrt{\tau}}\right)\right]+\frac{e^{-\eta}}{2}\left[\frac{\tau-\eta}{1+\gamma}+\frac{1}{1+\gamma^2}\right]\left[1+\Phi\left(\frac{\eta-\tau}{2\sqrt{\tau}}\right)\right]+\frac{(2+\gamma)\gamma}{2(1+\gamma)^2}e^{\frac{\tau+\eta}{\gamma}+\frac{\tau}{\gamma^2}}\left[1+\Phi\left(\frac{\eta+\tau}{2\sqrt{\tau}}+\frac{\sqrt{\tau}}{\gamma}\right)\right]. \quad (12)$$

$$\left(\frac{n-n^\circ}{n^\circ}\right)_{\eta=0}=-\frac{\sqrt{\tau/\pi}}{1+\gamma}e^{-\tau/4}-\frac{1}{2}\left[1+\Phi\left(\frac{\sqrt{\tau}}{2}\right)\right]+\frac{1}{2}\left[\frac{\tau}{1+\gamma}+\frac{1}{(1+\gamma)^2}\right]\left[1-\Phi\left(\frac{\sqrt{\tau}}{2}\right)\right]+\frac{(2+\gamma)\gamma}{2(1+\gamma)^2}e^{\frac{\tau}{\gamma}+\frac{\tau}{\gamma^2}}\left[1+\Phi\left(\frac{\sqrt{\tau}}{2}+\frac{\sqrt{\tau}}{\gamma}\right)\right] \quad (12a)$$

and for $\gamma=0$

$$\left(\frac{n-n^\circ}{n^\circ}\right)_{\gamma=0}=-\frac{\sqrt{\tau}}{\sqrt{\pi}}e^{-\frac{(\eta+\tau)^2}{2\sqrt{\tau}}}-\frac{1}{2}\left[1+\Phi\left(\frac{\eta+\tau}{2\sqrt{\tau}}\right)\right]+\frac{e^{-\eta}}{2}(\tau-\eta+1)\left[1+\Phi\left(\frac{\eta-\tau}{2\sqrt{\tau}}\right)\right] \quad (12b)$$

while for arbitrary $\gamma<0$

$$\frac{m}{n^\circ}=\frac{1}{2}-\frac{1}{\sqrt{\pi}}\int_0^{(\eta+\tau)/2\sqrt{\tau}}e^{-x^2}dx-\frac{e^{-\eta}}{\sqrt{\pi}(1+\gamma)}\int_{-\infty}^{(\eta-\tau)/2\sqrt{\tau}}e^{-x^2}dx+\frac{2+\gamma}{\sqrt{\pi}(1+\gamma)}e^{\frac{\eta+\tau}{\gamma}+\frac{\tau}{\gamma^2}}\int_{-\infty}^{(\eta+\tau)/2\sqrt{\tau}+\sqrt{\tau}/\gamma}e^{-x^2}dx \quad (12c)$$

The verification of the above equations by substitution into the differential equation and the boundary conditions is straightforward and is not reproduced in this report.

III. Description of Figures

In figure 1 there is shown the dependence of $(n-n)^\circ/n^\circ$ on τ at the cathode for a tube of infinite length. The curve for zero cathode volume ($\gamma=0$) is parabolic in shape at the origin. The initial rate at which the concentration builds itself up is seen to be very high. This is because the cathode has zero volume so that the initial rate is infinite. As time goes on the material concentrated at the end of the tube diffuses through a volume proportional to $\sqrt{\tau}$. The rate at which the concentrated material is being fed to this volume

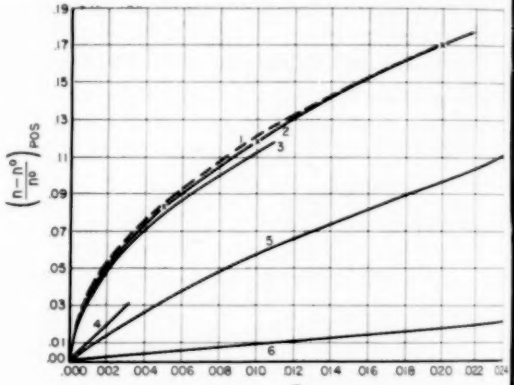

FIGURE 1.

$\lambda=\infty$, $n=0$; x *are points from* $\lambda=2$, $\gamma=0$, $\xi=2$.

1. Parabola $0.17\sqrt{\tau/.0200}$; 2. $\gamma=0$; 3. osculating parabola $2\sqrt{\tau/\pi}$; 4. tangent 5. $\gamma=0.1$; 6. $\gamma=1$

is proportional to τ and the concentration is therefore proportional to $\tau/\sqrt{\tau}=\sqrt{\tau}$. This is, of course, not an exact consideration, because the rate at which the concentrated material is being fed to the end of the tube depends on the concentration at neighboring places. The parabolic approximation is not bad, however, as is seen in figure 1, where the dotted curve above the curve for $\gamma=0$ is a parabola $0.17\sqrt{\tau/.0200}$, chosen so as to give a good overall fit and the dotted curve below the curve for $\gamma=0$ is the osculating parabola $2\sqrt{\tau/\pi}$. The latter curve makes a second-degree contact with the curve for $\gamma=0$. In figure 1 there are shown also, as crosses, points that correspond

to $\lambda=2$, $\xi=2$, $\gamma=0$. These are seen to fall on the curve $\lambda=\infty$, $\xi=2$, $\gamma=0$ to within the accuracy of the drawing. A close agreement of the two curves can be expected because the diffusion distance in natural units (D/a) is of the order $\sqrt{\tau}\sim 0.15$ for the larger τ in figure 1, while the length of the tube in the same units is 2. The time in figure 1 may thus be considered so short that the concentrated solution has not yet diffused to the anode. It is satisfactory in this case to make computations of the initial stage of the enrichment on the simplified assumption of an infinitely long tube ($\lambda=\infty$).

Figure 2 corresponds to negative a i. e. to the removal of ions from the cathode end. In this case $n-n^\circ$ is negative and, therefore, $-(n-n^\circ)/n^\circ$ is plotted as ordinate. A large ordinate corresponds to a small concentration in this figure and the cathode volume is zero. For $\tau=1$, the concentration is reduced to about 1/3 of its original value. The lower curve is drawn on an expanded time scale so as to show more detail in the initial value.

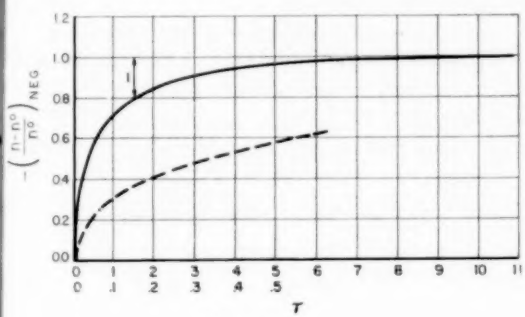

FIGURE 2.

$\lambda=\infty$, $\gamma=0$, $\pi=0$. 1. Remaining concentration divided by $n^\circ=\pi/n^\circ$

In figure 3 a comparison is made between the relative enrichment obtained by having the countercurrent balance exactly one or the other ion type that it is desired to separate. In this and some succeeding figures a positive a that corresponds to feeding an isotope into the cathode is referred to by the subscript "pos" and a negative a that corresponds to washing an isotope out of the cathode is similarly referred to by the subscript "neg". The lower curve in figure 3 corresponds to having the countercurrent of proper strength to balance the migration velocity of the slower isotope. If the initial concentrations of the more

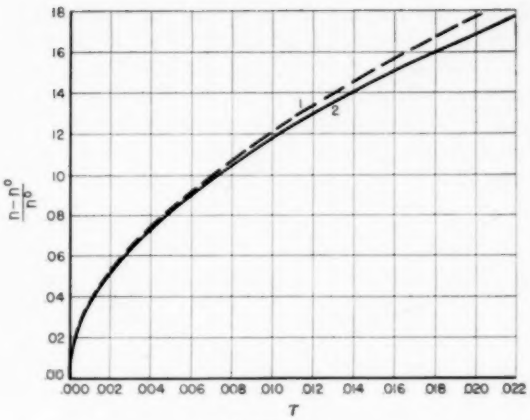

FIGURE 3.

$\lambda=\infty$, $\gamma=0$, $\pi=0$. 1. $\frac{1}{1+\left(\frac{n-n^\circ}{n^\circ}\right)_{neg}}-1$. 2. $\left(\frac{n-n^\circ}{n^\circ}\right)_{neg}$.

mobile and less mobile isotopes are n_l°, n_k° respectively, then at the time t this ratio is

$$\frac{n_l}{n_k}=\frac{n_l^\circ}{n_k^\circ}\left[1+\left(\frac{n-n^\circ}{n^\circ}\right)_{pos}\right] \tag{13}$$

and the factor by which this concentration is increased is unity, plus the quantity plotted for the lower curve.

If, on the other hand, the countercurrent is adjusted to balance the more mobile isotope, then the isotope of smaller migration velocity is being drawn out from the cathode and after a time t

$$\frac{n_l}{n_k}=\frac{n_l^\circ}{n_k^\circ\left[1+\left(\frac{n-n^\circ}{n^\circ}\right)_{neg}\right]}=\frac{n_l^\circ}{n_k^\circ}\left\{1+\left[-1+\frac{1}{1+\left(\frac{n-n^\circ}{n^\circ}\right)_{neg}}\right]\right\} \tag{13a}$$

The quantity in square brackets is plotted as the upper curve in figure 3. It represents, as before, the ratio of concentrations divided by its initial value and minus 1:

$$\frac{n_l/n_k}{n_l^\circ/n_k^\circ}-1.$$

It will be noted that for quite a while there is no marked difference in the two ways of adjusting the counter flow that have been considered.

In figure 4 five curves are shown. All of them are for a tube of infinite length. The lower pair

of curves is for $|\gamma|=0.1$. In this pair the upper curve corresponds to an adjustment of counter flow corresponding to eq 13a, the lower to an adjustment corresponding to eq 13. The less mobile isotope is being pumped out of the cathode for the upper curve, the more mobile isotope is being pumped into the cathode for the lower.

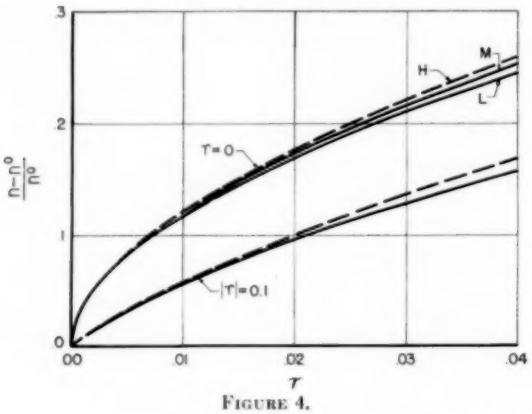

FIGURE 4.

$\lambda=\infty$, $\pi=0$. ———, $\left(\frac{n-n^\circ}{n^\circ}\right)_{pos}$; ·····, $\frac{1}{1+\left(\frac{n-n^\circ}{n^\circ}\right)_{neg}}-1$.

The three upper curves in figure 4 are for a tube of infinite length and zero cathode volume. Among these the highest curve, H, corresponds to countercurrent adjustment in eq 13a, the lowest to eq 13. The curve in between, curve M, corresponds to a countercurrent adjustment in which the arithmetic mean of the migration velocities of the more mobile and less mobile isotopes is equal to the velocity of the liquid.

The value of a for eq 13a is $-|\mu_l-\mu_h|E$ and for eq 13 it is $+|\mu_l-\mu_h|E$. In the computation for the middle curve in the upper set of three in figure 4 the value of a is $\pm|\mu_l-\mu_h|E/2$ and in accordance with eq 2e, the value of τ for a given t is ¼ of what it is for $a=\pm|\mu_l-\mu_h|E$. For this reason the abscissae for curve M were made to be 4τ. In this way the same value of the abscissae for the curves H, M, L corresponds to the same time, t.

The curve, M, was computed by plotting $[(n/n^\circ)_{pos}/(n/n^\circ)_{neg}]-1$ as ordinate and 4τ as abscissae. It is seen that the curve M falls nearly half way between H and L. This indicates that the exact adjustment of the countercurrent does not critically affect the ratio of the abundances of the two isotopes as long as there is an approximate balance of migration velocity and counter flow. With the idealized conditions assumed here the relative enrichment in the cathode is changed more rapidly by having the counter flow too high rather than too low.

The way in which the three typical adjustments of countercurrent give about the same result for small enrichments can be illustrated also in terms of a formula for small enrichments for $\gamma=0$. One has approximately

$$(n/n^\circ)_{pos}\cong 1+2\sqrt{\tau/\pi},\ (n/n^\circ)_{neg}\cong 1-2\sqrt{\tau/\pi}$$

so that

$$\left(\frac{n-n^\circ}{n^\circ}\right)_{pos}\cong\frac{1}{1+\left(\frac{n-n^\circ}{n^\circ}\right)_{neg}}-1\cong 2\sqrt{\tau/\pi}\quad (H,L$$

which shows the approximate equivalence of countercurrent adjustments, H and L. Also, for the countercurrent adjustments of the curve M

$$\frac{1+2\sqrt{\tau/\pi}}{1-2\sqrt{\tau/\pi}}-1\cong\frac{(n/n^\circ)_{pos}}{(n/n^\circ)_{neg}}-1\cong 2\sqrt{4\tau/\pi},\quad (M$$

so that the quantity M is the same function of 4τ as H, L are of τ.

For $V\neq 0$ a change in the countercurrent gives a change in γ. For small t the three types of countercurrent adjustment give nearly the same result. In this case

$$\left(\frac{n}{n^\circ}\right)_{pos}\cong 1+\frac{\tau}{|\gamma_0|}$$

where $\gamma_0=V(\mu_l-\mu_h)E/AD$. Similarly

$$\left(\frac{n}{n^\circ}\right)_{neg}\cong 1-\frac{\tau}{|\gamma_0|},$$

For the arithmetic mean countercurrent adjustment,

$$\frac{(n/n^\circ)_{pos}}{(n/n^\circ)_{neg}}-1\cong\frac{1+\frac{2\tau}{|\gamma_0|}}{1-\frac{2\tau}{|\gamma_0|}}-1=\frac{4\tau}{|\gamma_0|}$$

and the result is nearly the same as if the countercurrent were adjusted to keep one of the isotopes stationary with respect to the tube.

In figure 5 the behaviour of a tube of infinite length is compared with that of a tube of finite length in the special case of zero cathode volume. The concentration of an isotope at the cathode end is plotted against τ in both cases. The equilibrium concentration for the tube of finite length is taken to be $e^2=7.4$. Up to $\tau=2$, there is

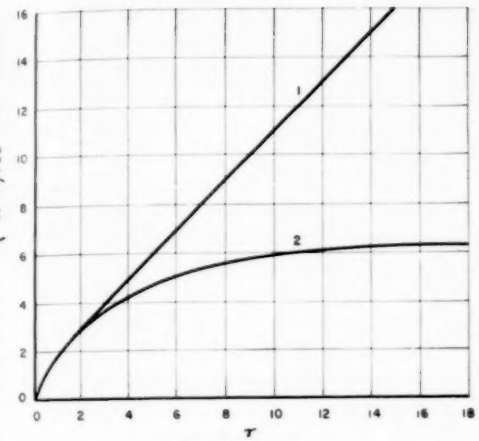

FIGURE 5.

$\gamma=0$, $n=0$. 1. $\lambda=\infty$. 2. $\lambda=2$.

not much difference between the two tubes. The concentration increases to about four times the initial value at this τ. For $\tau>4$, the slope of the curve for the tube of finite length decreases rapidly so that it will not pay to run above this value. The comparison of $\lambda=2$ with an infinitely long tube has already been made for small τ in figure 1. The initial stage of the divergence between the two curves can be seen in figure 6.

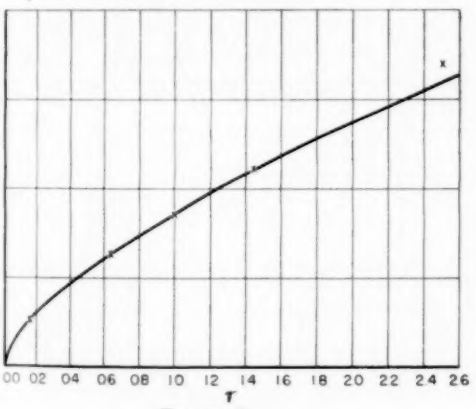

FIGURE 6.

$\gamma=2$, $\lambda=2$, $\xi=2$. x are for $\lambda=\infty$.

In figure 7 the dependence of concentration of a single isotope on τ is illustrated for $\gamma=0$ at different points along a tube of infinite length. The migration velocity is supposed to be greater than the countercurrent corresponding to a positive a. At the cathode end the concentration increases steeply, being proportional to $\sqrt{\tau}$ for small τ. For

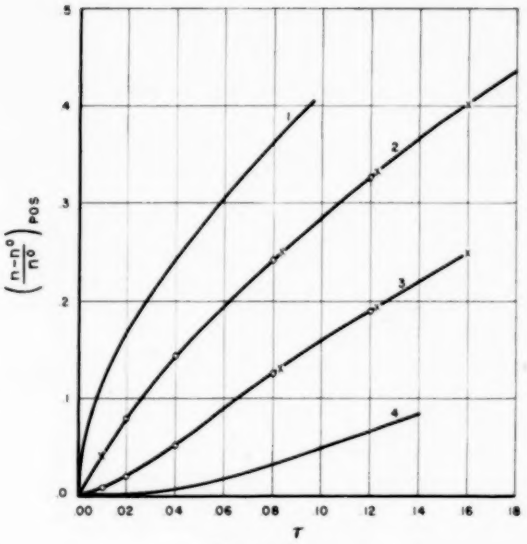

FIGURE 7.

$\gamma=0$. x are from $\lambda=\infty$; o are from $\lambda=2$. 1. $n=0.00$; 2. $n=0.10$, 3. $n=0.25$; 4. $n=0.50$.

points farther away from the cathode the initial portion of the curve is flat and is followed by an approximately linear rise. The initial flat stage can be thought of as corresponding to the time during which the concentration that first develops at the cathode diffuses to the point under consideration. In figure 7 there are also shown points that correspond to a tube of finite length with $\lambda=2$. These are seen to fall very closely on the curve for $\lambda=\infty$. This is to be expected, because for the small τ covered in this figure there is practically no effect at the anode end so that it does not matter whether the concentration at the anode is maintained at its initial value or not.

In figures 8 and 9 there is illustrated the varia-

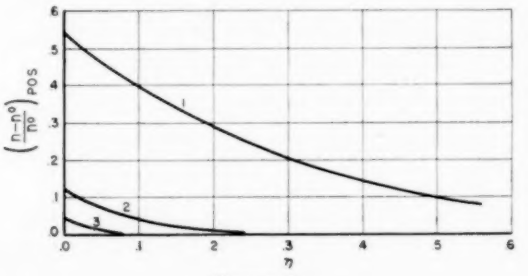

FIGURE 8.

$\gamma=0$. 1. $\tau=0.16$; 2. $\tau=0.010$; 3. $\tau=0.0016$.

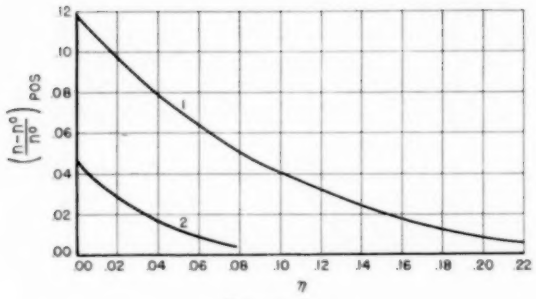

FIGURE 9.

$\gamma=0$. 1. $\tau=0.010$; 2. $\tau=0.0016$.

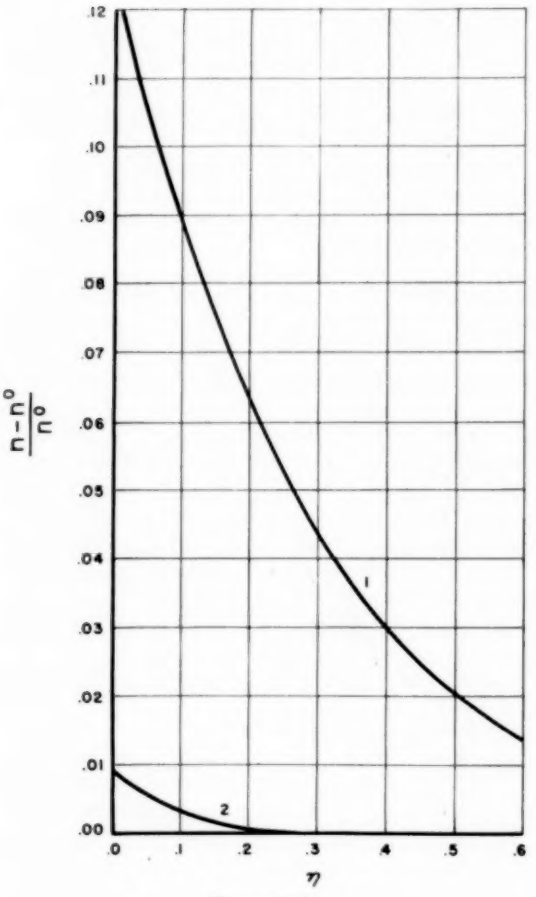

FIGURE 10.

$\gamma=1$, $\lambda=\infty$. 1 $\tau=0.16$ 2. $\tau=0.01$.

tion with distance of $[(n-n^\circ)/n^\circ]_{pos}$ i. e. of the fractional increase of concentration for the case of feeding the isotope towards the cathode. The cathode volume was taken to be zero for th figures, and the tube is infinitely long.

In figure 10 the variation of concentration w distance is illustrated for a finite cathode volu corresponding to $\gamma=1$. The tube is assum infinitely long and $a>0$ for this figure.

In figure 11 there is illustrated the variation concentration along the tube for the consta used in eq 9f. The computation can be made means of formula 9. The term $n^\circ e^\xi$ outside t sum is referred to as the "equilibrium ter The way in which the successive terms in t series converge is illustrated by the three curv The first curve is marked "equilibrium$+(r_0)$". represents the effect of the term $n^\circ e^\xi$ and of first term in the summation in eq 9. The seco curve is marked "equilibrium$+(r_0)+(\rho_1)$". includes, in addition to the two previous ter also the second term in the summation which due to the root ρ_1. This curve is already a approximation to the answer. The third cur includes the effect of the root ρ_2 and is mark "equilibrium$+(r_0)+(\rho_1)+(\rho_2)$". It is practica the answer. The special value, $\tau=0.16$, was us for all curves in this figure.

In figure 12 there is illustrated the superposit of terms for $\lambda=-1$, $\gamma=-8.1106$, $\tau=0.16$ as eq 9g.

In this case the isotope is being pumped out the cathode. The convention regarding label curves is the same as in figure 10. The converge

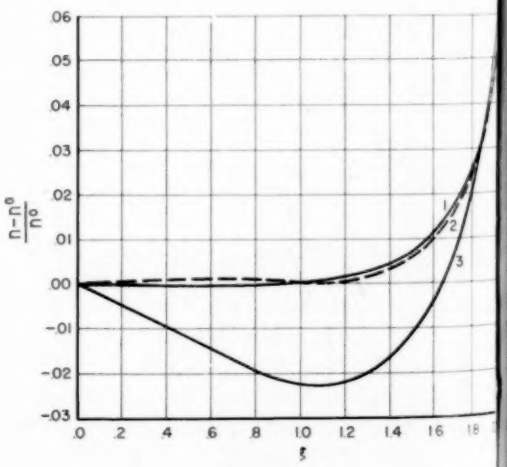

FIGURE 11.

$\lambda=2$, $\gamma=2.6696$, $\tau=0.16$. 1. Equilibrium$+(r_0)+(\rho_1)+(\rho_2)$; 2. equilibrium $(r_0)+(\rho_1)$. 3. equilibrium$+(r_0)$.

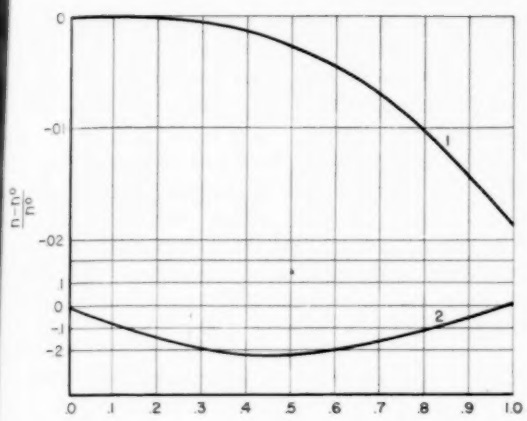

FIGURE 12.

$\lambda=-1$, $\gamma=-8.1106$, $\tau=0.16$. 1. Equilibrium+(r_0); 2. $(\rho_1)\times10^4$ contribution.

is very good. The curve for "equilibrium+(r_0)" is practically the answer. The contribution due to the term in ρ_1 multiplied by 10^4 is shown also in the lower part of the figure.

In figure 13 small λ and large γ are employed, $\lambda=1/5$ and $\gamma=24.022$. The convergence is so rapid that even at $\tau=0$ only the real root need be considered. For $\tau=1.6$, ten times the τ used in the two preceding figures, the distribution along the tube is not far from linear.

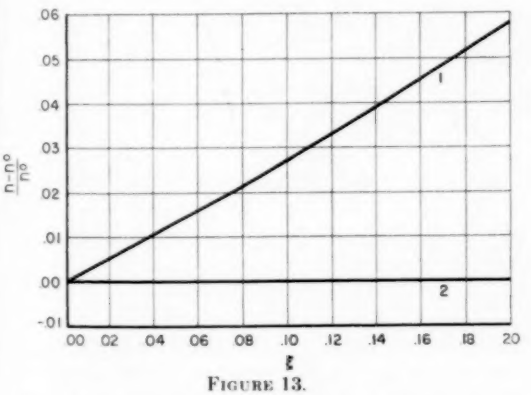

FIGURE 13.

$\lambda=2$, $\gamma=24.022$. Equilibrium term+(r_0) term in both curves. 1. $\tau=1.6$. 2. $\tau=0$.

IV. Discussion

1. Orders of Magnitude.

It appears possible that the difference in mobilities is of the order of $(\sqrt{M_h/M_l}-1)\mu$ where μ is the mobility and M_h, M_l are the masses of the ions. For K^+, the experimental value of μ is $\sim 6.6\times10^{-4}\frac{\text{cm}^2}{\text{v-sec}}$. The effect of convection on D_h, D_l due to thermal effects is not known. A lower limit for D_l, D_h can be obtained from the relations

$$\mu_l=\frac{e}{kT}D_l,\ \mu_h=\frac{e}{kT}D_h$$

which follow from statistical mechanics. Here e is the ionic charge and not the electronic charge. For a singly charged ion, e is minus the charge on the electron. At room temperatures for singly charged ions the above formulas give

$$D=.026\mu\left(D \text{ in } \frac{\text{cm}^2}{\text{sec}};\ \mu \text{ in } \frac{\text{cm}^2}{\text{v-sec}}\right)$$

For a countercurrent adjusted to balance the slower ion one has, assuming

$$\mu_l-\mu_h=\frac{6.6\times10^{-4}}{200}=3.3\times10^{-6}\ \frac{\text{cm}^2}{\text{v-sec}}$$

$$a=3.3\times10^{-6}E$$

where E is in v/cm. Hence

$$\xi=\frac{3.3\times10^{-6}}{1.7\times10^{-5}}Ex=0.2Ex.$$

A change in ξ by 1 corresponds in this case to a drop of 5 v along the tube. More generally, for the same countercurrent adjustment, and singly charged ions

$$\xi_l=\frac{\Delta\mu}{\mu}\frac{eEx}{kT}=39\frac{\Delta\mu}{\mu}\text{ times voltage drop}$$

Here $\Delta\mu$ is the absolute value of the difference in mobilities. Thus if $\Delta\mu/\mu=1/1{,}000$ then 26 v are required to change ξ by unity and to give a factor, e, in the concentration in equilibrium.

The quantity τ can be considered as the time in units D/a^2. For K^+ this unit is of the order

$$\frac{1.7\times10^{-5}}{(3.3)^2\times10^{-12}E^2}=1.6\times10^6\text{ sec}/E^2=430\text{ hr}/E^2$$

where E is in v/cm and the countercurrent adjustment is such as to keep one of the ions stationary. In the example of figure 5 one may consider $\tau\sim2$ as corresponding to the time which it takes to reach half equilibrium, and the time constant is in this

case of the order 1,000 hr/E^2. More generally the natural unit of time is

$$\frac{D}{(\Delta\mu)^2 E^2}$$

On account of the large uncertainty in $\Delta\mu$ for uranium this unit cannot be computed with certainty. Since $\Delta\mu$ enters to the square, a decrease in $\Delta\mu$ by a factor 10 brings about an embarrassing increase of a factor 100 in the time unit. For a small cathode volume i. e. for small γ, the "natural" unit of time is the main thing that matters so that a sufficiently large $\Delta\mu$ is then especially important for a small time constant.

On the other hand, if γ is large the value of τ corresponding to half equilibrium is much greater than unity as is seen in the examples following eq 9e. According to eq 8c for a fixed λ, the difference of mobility enters only once in the denominator in this case. For K^+ assuming $\Delta\mu=\mu/_{200}$ and taking $V=20$ cm^3, $A=1$ cm^2 the time constant is

$$\frac{6\times10^6 \text{ sec.}}{E}(e^\lambda-1)=\frac{2{,}000 \text{ hr}}{E}(e^\lambda-1)$$

It is interesting to note that if the equilibrium enrichment factor e^λ is kept fixed and if γ is large enough to make formula 8b applicable then the time constant does not depend on the diffusion constant, D, but only on the difference of mobility $\Delta\mu$. In order, however, that λ be fixed for different D and E, one has to vary the length, L. For a tube 30 cm long with 90 v applied having a free cross-sectional area 1 cm^2 and a cathode volume $V=20$ cm^3, one has in the absence of convection and for $\Delta\mu/\mu=1/_{200}$, $\lambda=17.5$, $\gamma=12$. An enormous equilibrium concentration of e^{17} could be obtained in theory in such a case, but it would also take an impractical time to approach this equilibrium. It is doubtful, however, that D can be as small as assumed $\left(1.7\times10^{-5}\frac{\text{cm}^2}{\text{sec}}\right)$ because of the convection currents.

The values $\lambda=2$, $\gamma=2.6995$, (used in example of 9f) in the absence of convection for $\Delta\mu/\mu=1/_{200}$ correspond to 10 v applied to the tube. If the tube is 30 cm long and has a free cross-sectional area of 1 cm^2, the cathode compartment would have to be 40 cm^3. One has $a=3.3\times10^{-6}/3=1.1\times10^{-6}$ cm/sec and $V/A=40$ cm so that $T=3\times10^8$ sec $\sim10^5$ hr which is of the order of 5,000 days. If this tube were shortened to 3 cm keeping V and A constant and the same voltage then λ remains unchanged and a is increased by a factor 10 so that T decreases to about 500 days.

There is a large gain in the shortened time constant due to shortening the tube for the same voltage. This is because of the increased current. The gain is of no real help except through the increased current and the detection of a difference in ionic mobilities appears to be easiest with a large current in a long tube.

2. Equilibrium Concentration

In this section the coefficients of diffusion will be decomposed into a part present in the stagnant liquid and a part due to spurious causes such as convection and stirring.

$$D_l=D_l^\circ+\mathfrak{D},\ D_h=D_h^\circ+\mathfrak{D}.$$

It is supposed that the spurious effects give the same contribution $\mathfrak{D}$ to D_l and D_h. The relations

$$\mu_l=\frac{e}{kT}D_l^\circ,\ \mu_h=\frac{e}{kT}D_h^\circ$$

hold. In equilibrium

$$\frac{n_l}{n_h}\frac{n_h^\circ}{n_l^\circ}=e^\alpha,$$

where

$$\frac{\alpha}{L}=\frac{\mu_l E+v}{\mathfrak{D}+D_l^\circ}-\frac{\mu_h E+v}{\mathfrak{D}+D_h^\circ}=\frac{D_h^\circ-D_l^\circ}{(\mathfrak{D}+D_l^\circ)(\mathfrak{D}+D_h^\circ)}\left(v-\frac{eE}{kT}\mathfrak{D}\right).$$

The counter current is supposed to be adjusted so that

$$v=-\mu_h E(1+\theta)$$

If $\theta=0$, then isotope h is kept stationary by the combined action of the countercurrent and of the migration velocity. However, θ will not be supposed to be necessarily zero. One has* from the above equations,

$$\alpha=\frac{e\mathfrak{E}L}{kT}[\mathfrak{D}+D_h^\circ(1+\theta)]\frac{D_l^\circ-D_h^\circ}{(\mathfrak{D}+D_h^\circ)(\mathfrak{D}+D_l^\circ)}$$

*Prof. H. C. Urey first derived a special case of the above formula which corresponds to $\mathfrak{D}=0$, $\theta=0$. The authors are indebted to Prof. Urey for a stimulating discussion in this connection.

For $\mathfrak{D}=0$ one has

$$\alpha=\frac{eEL}{kT}(1+\theta)\frac{D_l^\circ-D_h^\circ}{D_l^\circ}=$$

$$\frac{eEL}{kT}(1+\theta)\frac{\mu_l-\mu_h}{\mu_l}\quad(\mathfrak{D}=0)$$

Here at room temperatures

$$\frac{eEL}{kT}=39\ x\ \text{applied voltage}\times\text{valence}$$

just as for the quantity ξ. It is seen from the above formula for α that a large θ is advantageous for getting a large enrichment ratio. This fact should perhaps be emphasized because it indicates that it is better to have the countercurrent too strong rather than too weak if it is desired to test for the existence of a mobility effect.

If $\mathfrak{D}>>D^\circ$, one has

$$\alpha=\frac{e\mathfrak{E}L}{kT}\frac{D_l^\circ-D_h^\circ}{\mathfrak{D}}=\frac{e\mathfrak{E}L}{kT}\frac{\mu_l-\mu_h}{\mu_l}\frac{D^\circ}{\mathfrak{D}}\quad(\mathfrak{D}>>D^\circ)$$

For large $\mathfrak{D}$ the logarithmic increment is seen to be a fraction $D^\circ/\mathfrak{D}$ of its value for $\mathfrak{D}=0$, $\theta=0$. In this limit the exact adjustment of the counter current is of no importance for the enrichment factor at equilibrium.

V. References

[1] A. Keith Brewer, S. L. Madorsky, and J. W. Westhaver, Science **104**, 156 (1946).

[2] A. Keith Brewer, S. L. Madorsky, John Keenan Taylor, Vernon H. Dibeler, J. Research NBS **38**, 137 (1947) RP1765.

[3] Samuel L. Madorsky and Sidney Straus, J. Research NBS **38**, 169 (1947) RP1766.

[4] Jahnecke, Emde, Tables of functions with formulae and curves, p. 3 (B. G. Teubner, Leipzig, 1909).

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Activity Coefficients in Aqueous Mixtures of Phosphates with Sodium Chloride, Sodium Bromide, and Sodium Iodide, and the pH of Phosphate Buffer Solutions

By Roger G. Bates

The electromotive force of cells with hydrogen electrodes and silver-silver bromide or silver-silver iodide electrodes was measured at 25° C. The electrolyte in each cell consisted of an aqueous mixture of (a) potassium dihydrogen phosphate, (b) disodium hydrogen phosphate, and (c) sodium bromide or sodium iodide. The molalities of (a) and (b) were always equal, whereas the ratio of the molality of (c) to that of (a) or (b) was 1, 0.5, or 0.2. The ionic strengths ranged from 0.04 to 0.25. The data are compared with similar measurements for phosphate-chloride mixtures reported in an earlier paper. At a given ionic strength, the activity-coefficient term, $f_{H_2PO_4}f_X/f_{HPO_4}$ where X represents halide, increases when bromide at a given concentration is substituted for chloride at the same concentration, or when iodide replaces bromide. Accurate values for the pH of phosphate buffer solutions with and without added salt can be obtained only at low ionic strengths.

I. Introduction

During the past several years, methods for determining activity pH ($-\log \mathbf{a}_H$) for standard buffer solutions from electromotive-force measurements of cells without liquid junction have been developed. These methods have been used to assign pH values to certain phosphate, phthalate, and borate solutions prepared from Standard Samples certified by the National Bureau of Standards [1, 2, 3].[1] Cells with hydrogen and silver-silver chloride electrodes were employed in each instance. The electromotive-force data for aqueous mixtures of the buffers with sodium or potassium chloride afford an unequivocal determination of $-\log \mathbf{a}_H f_{Cl}$, where f_{Cl} is the activity coefficient of chloride ion[2] for each solution studied. Furthermore, the value of this quantity in a buffer solution without chloride can be ascertained by a suitable extrapolation from a series of determinations in which the molal ratio of chloride to buffer is varied. It is impossible to derive $-\log \mathbf{a}_H$ from these measurable quantities without an estimate of f_{Cl}, and the evaluation of this ionic activity coefficient must rest partly upon arbitrary considerations. It must be realized that paH computed from the emf of cells without liquid junction is primarily a unit on an arbitrary scale, as is that determined by the usual pH assembly with a liquid junction [5, 6]. Its significance in terms of thermodynamic constants may be limited to a small number of standard solutions of assigned paH and may not be imparted to mixtures of unknown composition whose paH it is desired to determine.

The chloride ion plays a unique and important role in the derivation of paH from the emf of the hydrogen-silver chloride cell without junction. However reasonable the assumptions involved in the computation may appear, their validity can usually not be affirmed. Hence, it is important to demonstrate the extent to which the properties of chloride ion, and of the silver-silver chloride electrode, influence the paH of the buffer solution without chloride obtained by these means. For this purpose, equimolal mixtures of potassium

[1] Figures in brackets indicate the literature references at the end of this paper.

[2] The molal scale of activity is used throughout this paper. The so-called "activity pH", $-\log \mathbf{a}_H$, will be designated paH, in accordance with the suggestion of Sørensen and Linderstrøm-Lang [4]. Concentrations will be given in molality (m). The symbol μ is used for ionic strength.

dihydrogen phosphate and disodium hydrogen phosphate were chosen. The paH of these solutions has already been calculated from measurements of $-\log \mathbf{a}_H f_{Cl}$ in mixtures of the phosphate buffer with varying amounts of sodium chloride [1]. Sodium bromide and sodium iodide were added to equimolal phosphate buffers in such amounts that the ratios of the molality of halide to that of each phosphate had the three values 1, 0.5, and 0.2. Measurements of the emf of hydrogen-silver bromide and hydrogen-silver iodide cells, with these phosphate-halide mixtures as cell solutions, were made at 25° C. The assumptions were tested by computing the paH of the phosphate buffer, in the absence of added salt, from the three series of emf data.

II. Determination of the Activity Coefficients

The cells used in this study can all be represented by the following scheme,

$$\mathrm{Pt;\ H_2(g,\ 1\ atm),\ KH_2PO_4}(m_1),\ \mathrm{Na_2HPO_4}(m_1),\ \mathrm{NaX}(m_2),\ \mathrm{AgX}(s);\ \mathrm{Ag},$$

where X is chloride, bromide, or iodide, and m is molality. When the standard potential, $E°$, of the cell is known, $-\log \mathbf{a}_H f_X$ is readily obtained from the emf, E, and natural constants:

$$-\log \mathbf{a}_H f_X = -\log (f_H f_X m_H) = \frac{(E-E°)\mathbf{F}}{2.3026RT} + \log m_X. \tag{1}$$

In eq 1, $\mathbf{F}$ is the faraday, R the gas constant, and T the absolute temperature. By substitution of the equilibrium constant for the second dissociation of phosphoric acid in eq 1, we obtain an equation for the activity-coefficient term, designated $\log f_r$,

$$\log f_r \equiv \log \frac{f_{H_2PO_4} f_X}{f_{HPO_4}} = pK - \frac{(E-E°)\mathbf{F}}{2.3026RT} - \log m_X - \log \frac{m_{H_2PO_4}}{m_{HPO_4}}, \tag{2}$$

where pK is the common logarithm of the reciprocal of K, the second dissociation constant [1, 7]. In all of the phosphate buffers to be discussed, the last term of eq 2 is zero.

1. Experimental Procedures

Preparation of the equimolal mixture of so potassium dihydrogen phosphate and disodiu hydrogen phosphate was described by Bates a Acree [1]. Sodium bromide was recrystalliz three times from water and was dried at 200° 300° C. The dry product was found to be neutr Sodium iodide was recrystallized twice from wat and dried in vacuum at 50° C for 1 to 2 day Filters of sintered glass were used in each instan for separating the crystals from the saturat solution.

Silver-silver bromide electrodes were made described by Keston [8]. However, the paste silver oxide and silver bromate was decompos at 550° C instead of at 650° C. Silver broma was prepared from sodium bromate and silv nitrate. It was recrystallized from hot wate Silver-silver iodide electrodes were formed platinum spirals by thermal decomposition, at 45 C, of a paste composed of 90 percent of silv oxide and 10 percent of silver iodide by weigh [9]. Silver iodide, prepared from silver nitra and recrystallized potassium iodide, was washe 40 times with water and digested at 70° C unde water for 2 days. Hydrogen electrodes wer made by deposition of platinum black on plati num foils sealed in glass. A 3-percent solution of chloroplatinic acid that contained a smal amount of lead acetate was used, and the electrolysis was continued for 3 minutes at a current o 250 to 300 ma. Electrodes were always used i pairs and were freshly made for each cell.

The solutions were prepared by weight methods and nitrogen was passed through them to remov air. Details of the cells and of a part of th equipment are given in an earlier publication [7] Some of the temperature measurements were made with a platinum resistance thermometer and the rest with a calibrated mercury thermometer. The temperature was regulated within ±0.0 deg C.

The titration cell already described [10] was used for a part of the measurements made with hydrogen and silver-silver bromide electrodes. For this purpose, "semimicro" silver-silver bromide electrodes were prepared. The mixture of silver and silver bromide on each electrode weighed 15 to 20 mg. The cell was immersed in the constant-temperature bath and a known

amount of buffer-bromide mixture added. When the emf had become constant, usually in about 2 hours, a measured portion of air-free water was introduced from the burette. Occasionally a second dilution was made. The emf data for the seven solutions prepared by dilution within the cell are not considered to be as accurate as the rest. These measurements are therefore marked for identification in the table of results given in the next section.

The measuring equipment was checked in two ways. The potentiometer was connected with another similar instrument in the same laboratory, and the emf of a cell was occasionally measured by both instruments. The two values always agreed within 0.02 mv. The potentiometers and standard cells had been calibrated by this Bureau. The second method offered a comparison of the silver-silver chloride electrodes with those of Harned and Ehlers [11], for which the standard potential of this electrode was derived. It furnished, as well, an additional check upon the temperature control and on the accuracy of the potentiometer. The emf of three hydrogen-silver chloride cells that contained 0.09931m of hydrochloric acid was measured and found to be 0.35272 ± 0.00002 v at 25° C. This value is identical with that obtained by interpolation in the data of Harned and Ehlers.

2. Results and Calculations

The experimental data are summarized in tables 1 and 2. Values of $-\log (f_H f_X m_H)$, where X represents either bromide or iodide, are given in the last columns. They were calculated from the emf by eq 1.

The standard potential, $E°$, of the hydrogen-silver bromide cell was taken to be 0.07128 v at 25° C [12]. For the hydrogen-silver iodide cell, the emf data of table 2, together with $pK=7.198$ [1, 7], yield, by the method of Owen [13], −0.15201 v for $E°$. This potential was used in the subsequent computations. Owen [13] found −0.15225 for the same cell with silver-silver iodide electrodes formed by the thermal decomposition of a mixture of silver oxide and silver iodate. Gould and Vosburgh [14], however, obtained −0.1519. Their electrodes were of the same type as those used in this investigation.

Values of $-\log (f_H f_X m_H)$ for solutions that contained sodium bromide and sodium iodide at a

TABLE 1. *Emf of the cell*, Pt; H_2 (1 atm), KH_2PO_4 (xm_1), Na_2HPO_4 (xm_1), NaBr (xm_2), AgBr (s); Ag, at 25° C; *values of* $-\log (f_H f_{Br} m_H)$

x	E_{25}	$-\log (f_H f_{Br} m_H)$
SERIES A: $m_1=m_2=0.05$		
	Volt	
1	0.55418	6.864
0.9438	.55601	6.870
0.5606	.57237	6.924
0.4172 [a]	.58211	6.957
0.3809	.58487	6.963
0.1882	.60625	7.019
SERIES B: $m_1=2m_2=0.05$		
1	[b] 0.57322	6.885
0.8486	.57815	6.897
0.6544	.58666	6.928
0.5218 [a]	.59343	6.945
0.4984 [a]	.59523	6.955
0.3506	.60570	6.979
0.2468 [a]	.61647	7.009
SERIES C: $m_1=5m_2=0.05$		
1	[c] 0.59731	6.895
0.8070	.60417	6.918
0.6600 [a]	.61051	6.937
0.5240	.61754	6.956
0.4922 [a]	.61966	6.965
0.4316 [a]	.62338	6.971

[a] Dilution made in a titration cell.
[b] Average of two cells. Mean deviation, 0.09 mv.
[c] Average of three cells. Mean deviation, 0.04 mv.

TABLE 2. *Emf of the cell*, Pt; H_2 (1 atm), KH_2PO_4 (xm_1), Na_2HPO_4 (xm_1), NaI (xm_2), AgI (s); Ag, at 25° C; *values of* $-\log (f_H f_I m_H)$

x	E_{25}	$-\log (f_H f_I m_H)$
SERIES D: $m_1=m_2=0.05$		
	Volt	
1	[a] 0.33036	6.856
0.5616	[a] .34898	6.920
0.3228	[a] .36620	6.971
0.1606	[a] .38753	7.028
SERIES E: $m_1=2m_2=0.05$		
1	0.34925	6.874
0.4594	.37387	6.952
0.3314	.38402	6.982
SERIES F: $m_1=5m_2=0.05$		
1	0.37355	6.887
0.6462	.38749	6.933
0.4090	.40183	6.977
0.3006	.41116	7.001

[a] Average emf of two cells. The differences between duplicate cells made from these four solutions were 0.07, 0.17, 0.07, and 0.04 mv.

molality equal to that of each phosphate salt are compared with similar data for phosphate-chloride mixtures [1] in figure 1. When the three curves, plotted from measurements at sufficiently high concentrations that the buffer ratio was always unity, are extended to zero ionic strength, they meet at 7.198, the value of pK at 25° C. The separation of these three curves at a given ionic strength decreases as the ratio of halide to phosphate decreases, but the curves fail to meet, if the ionic strength exceeds 0.05, even at zero concentration of halide.

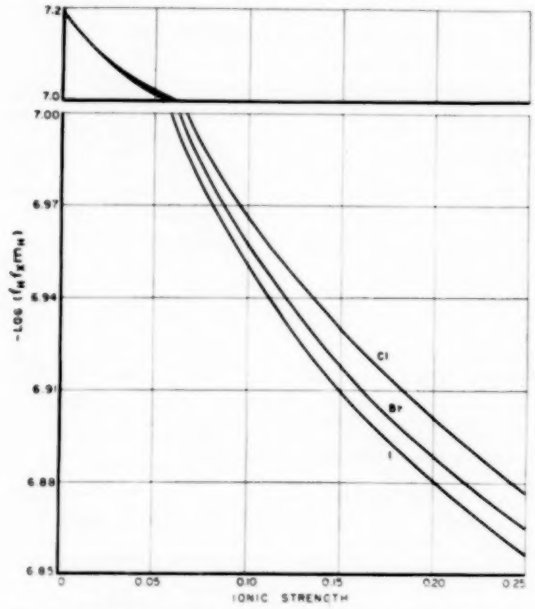

FIGURE 1. *Values of* $-\log (f_H f_X m_H)$ *in equimolal phosphate buffers containing sodium halide* (NaX) *at a molality equal to that of each phosphate, plotted as a function of ionic strength.*

The activity-coefficient term, $\log (f_{H_2PO_4} f_X / f_{HPO_4})$, was computed by eq 2. The values obtained in this manner for each ratio of bromide and iodide to phosphate were smoothed with the aid of plots of P, defined by

$$P \equiv \log f_r - 1.017\sqrt{\mu}/(1+1.31\sqrt{\mu}), \qquad (3)$$

as a function of ionic strength, μ. These lines were drawn to the origin, inasmuch as P is zero at infinite dilution. Their curvatures were small. The average deviation, Δ, of the "observed" log f_r from the smooth curve is given in the next to the last column of table 3. These deviations, expressed in millivolts, are designated Δ' and are listed in the last column. The value of log f_r in phosphate buffer solutions with varying amounts of sodium chloride, sodium bromide, or sodium iodide, and in buffer solutions without halide (log f_r°), is given in table 4. Log f_r in mixtures

TABLE 3. *Smoothing of log* f_r

Series	m_X/μ	Number of solutions	Δ	Δ'
PHOSPHATE-BROMIDE MIXTURES				
				mv
A	0.2	6	0.0009	0.05
B	.11	7	.0026	.15
C	.048	6	.0014	.08
PHOSPHATE-IODIDE MIXTURES				
D	0.2	4	0.0006	0.04
E	.11	3	.0002	.01
F	.048	4	.0014	.08

TABLE 4. *Log* f_r, *log* f_r°, *and* $-\log (f_H f_X m_H)^\circ$ *for phosphate buffer solutions*

Ionic strength	log f_r when m_{NaX}/μ is—			log f_r°	$-\log (f_H f_X m_H)^\circ$
	0.2	0.11	0.048		
X=Cl					
0.01				0.089	7.109
.05	0.1770	0.1760	[a]0.1749	.1748	7.023
.07	.2018	.2004	.1989	.1983	7.000
.1	.2310	.2290	.2268	.2263	6.972
.15	.2679	.2649	.2616	.2610	6.937
.20	.2968	.2926	.2884	.2870	6.911
.25	.3209	.3156	.3103	.3084	6.890
X=Br					
0.01				0.090	7.108
.05	0.1818	0.1802	0.1782	.1772	7.021
.07	.2080	.2058	.2035	.2020	6.996
.1	.2391	.2360	.2330	.2310	6.967
.15	.2786	.2739	.2699	.2672	6.931
.20	.3091	.3032	.2986	.2952	6.903
.25	.3340	.3270	.3220	.3183	6.880
X=I					
0.01				0.091	7.107
.05	0.1839	0.1836	0.1808	.1790	7.019
.07	.2132	.2105	.2067	.2048	6.993
.1	.2453	.2421	.2372	.2350	6.963
.15	.2857	.2817	.2759	.2730	6.925
.20	.3170	.3116	.3058	.3028	6.895
.25	.3425	.3357	.3306	.3267	6.873

[a] Values of log f_r in the phosphate-chloride mixtures are given for m_{NaCl}/μ = 0.03 instead of 0.048.

that contained bromide or iodide was read from the smoothed curves and for chloride-phosphate mixtures was taken from data given in the earlier paper [1]. The limiting values, $\log f_r^\circ$, were obtained from plots of $\log f_r$ with respect to m_X/μ, as shown in figure 2. Straight-line extrapolations were used.

The estimated accuracy of the emf of the bromide and iodide cells is about 0.10 mv. The combined errors in emf, in choice of the proper standard potentials for these types of electrodes, and in smoothing and extrapolating $\log f_r$ require that the limiting quantity, $\log f_r^\circ$, be assigned uncertainties of ± 0.002 for the chloride series and ± 0.003 for the bromide and iodide series.

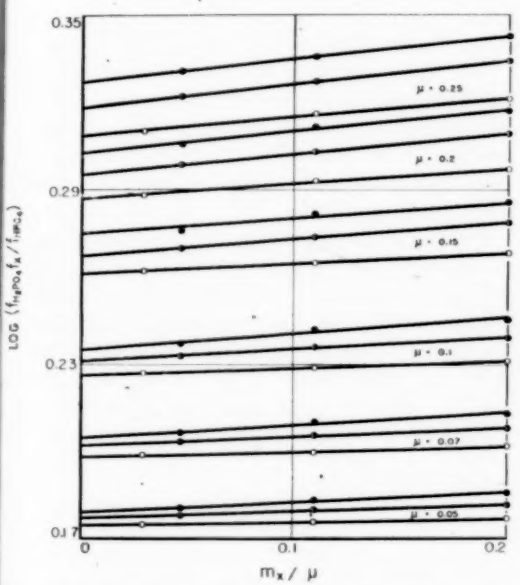

FIGURE 2. *Log* $(f_{H_2PO_4}f_X/f_{HPO_4})$ *plotted as a function of the fractional contribution of halide, NaX, to the total ionic strength.*

Lower curve of each group: X is Cl; middle curve: X is Br; upper curve: X is I

The last column of table 4 gives the limiting value of $-\log (f_H f_X m_H)$, when halide is absent, at each ionic strength. Inasmuch as the ratio of the molalities of the two phosphate anions remains unity, $-\log (f_H f_X m_H)^\circ$ is obtained simply by subtraction of $\log f_r^\circ$ from pK:

$$-\log (f_H f_X m_H)^\circ = pK - \log f_r^\circ \qquad (4)$$

Equation 4 is readily derived from the mass law and the definition of f_r (eq 2).

It is noteworthy that $-\log (f_H f_X m_H)^\circ$ decreases as X increases in atomic weight. This change is to be expected if the activity coefficients of the halogen acids at zero concentration in a phosphate solution are in the same order as the mean activity coefficients of the sodium and potassium halides and the halogen acids in their pure aqueous solutions. For the same reason, $\log f_r^\circ$ increases from chloride to iodide. The employment of these activity coefficients in the estimation of the paH of phosphate buffer solutions will be considered in the next section.

III. pH of Phosphate Buffer Solutions

Bates and Acree [1] found that the change of $\log f_r$ with ionic strength for each of the ratios of chloride to phosphate could be represented satisfactorily by an equation of the Hückel [15] type with two adjustable parameters, a^* and β^*. Log f_r° at 25° C can be expressed by the equation,

$$\log f_r^\circ = \frac{1.017\sqrt{\mu}}{1+0.3281\ a^\circ\sqrt{\mu}} + \beta^\circ\mu. \qquad (5)$$

The values of a° and β° for the chloride, bromide, and iodide series were determined by fitting $\log f_r^\circ$, given in table 4, to eq 5. The parameters, obtained by least-square methods, are listed in table 5. The average difference, Δ, between the "observed" $\log f_r^\circ$ and that calculated by eq 5 is given in the last column.

TABLE 5. *Parameters of eq 5 for log* $(f_{H_2PO_4}f_X/f_{HPO_4})$ *in phosphate buffers without halide*

	a°	β°	Δ
Cl	4.4	0.054	0.0002
Br	4.2	.069	.0000
I	4.0	.079	.0003

Up to this point, the treatment has remained thermodynamically rigorous. However, an evaluation of paH, or $-\log f_H m_H$, will involve an assumption that is partly arbitrary, as indicated earlier in this paper. The formal mass-law expression for the paH of a phosphate buffer solution, with substitution of the Hückel equation

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for the activity coefficients of the two phosphate anions at 25° C, can be written as follows,

$$\text{paH} = \text{p}K - \log \frac{m_{H_2PO_4}}{m_{HPO_4}} - \frac{1.5255\sqrt{\mu}}{1+0.3281a\sqrt{\mu}} - \beta\mu. \quad (6)$$

Bates and Acree assumed that a° and β°, the parameters of eq 5 for phosphate buffers without added chloride, could be identified with a and β of eq 6, for the same buffer solutions.[3] The validity of this assumption is not subject to experimental proof, but a partial test can be obtained through a comparison of the paH derived in this manner from emf measurements made with the three different halide electrodes. The results of these calculations are given in the first half of table 6. At 0.25, the highest ionic strength studied, the paH values derived from measurements of the chloride and iodide cells differ by 0.025 unit.

It is evident from a comparison of paH with $-\log (f_H f_X m_H)^\circ$ given in table 4 that the normal decrease of the latter quantity with increasing atomic weight of the halogen has not been compensated; indeed paH shows a slightly larger decrease than does $-\log (f_H f_X m_H)^\circ$ at the same ionic strength. A part of the difficulty is associated with the two-parameter form of eq 5. If a small systematic change, within experimental error, were made in $\log f_r^\circ$, significant changes in a° and β° of a compensatory nature might be necessary to afford the best fit of the data to eq 5. For example, $a^\circ = 4.0$ and $\beta^\circ = 0.079$ reproduce $\log f_r^\circ$ for the iodide series with a mean deviation of 0.0003. Yet the deviation would be only 0.0006 or still considerably less than the uncertainty assigned to $\log f_r^\circ$, if 4.4 and 0.135 were chosen as the correct set of parameters. If the latter values gave the best fit, however, the paH computed from the iodide series would be 0.006 unit higher at an ionic strength of 0.25. In other words these changes in the two parameters do not offset one another in the calculation of paH. Measurements at ionic strengths above 0.25, which are of most use in fixing accurate values of the parameters, are lacking here.

TABLE 6. paH *of phosphate buffer mixtures:* $KH_2PO_4(m_1)$, $Na_2HPO_4(m_1)$, $NaX(m_2=0)$, *from the emf of cells without liquid junction at 25° C*

m_1	Ionic strength	paH when X is—		
		Chloride	Bromide	Iodide
Equation 6				
0.0025	0.01	7.065	7.063	7.062
.005	.02	7.017	7.016	7.014
.01	.04	6.959	6.956	6.953
.0125	.05	6.937	6.934	6.931
.025	.10	6.862	6.855	6.849
.0375	.15	6.811	6.803	6.794
.05	.20	6.773	6.762	6.752
.0625	.25	6.742	6.729	6.717
Equation 7				
.0025	0.01	7.066	7.065	.....
.005	.02	7.019	7.020	.....
.01	.04	6.962	.....	.....
.0125	.05	6.942	6.944	.....
.025	.10	6.873	6.873	6.876
.0375	.15	6.830	6.829	6.834
.05	.20	6.796	6.796	6.802
.0625	.25	6.774	6.774	6.781

[3] The last two terms of eq 6 represent $-\log (f_{H_2PO_4}/f_{HPO_4})^\circ$. It is evident by comparison with eq 5 that this method of evaluating paH sets $\log f_X^\circ$ equal to $-0.5085\sqrt{\mu}/(1+0.3281a^\circ\sqrt{\mu})$, without a term linear in ionic strength.

If the activity-coefficients of the three halide ions in the phosphate solution were assumed to equal the mean activity coefficients of the corresponding halogen acids, after the suggestion of Guggenheim [16], and these mean activity coefficients were set equal to their values in pure solutions of HX [11, 17, 18] at the appropriate ionic strengths, paH could be evaluated:

$$\text{paH} = -\log (f_H f_X m_H)^\circ + \log f_X^\circ \equiv -\log (f_H f_X m_H)^\circ + \log f_{HCl} \quad (7$$

The results of this calculation are given in the second half of table 6. The agreement among the three sets of values is improved, but the paH is higher than before. The activity coefficient of hydrochloric acid is lowered by potassium ions [19] and sodium ions [20]. Hence, paH computed in this manner is understandably too high.

The paH calculated from pK or from $-\log (f_H f_X m_H)^\circ$ will approach $-\log \mathbf{a}_H$ in dilute solutions, where all reasonable assumptions relating the ionic activity coefficients yield substantially equivalent results. In the region of higher ionic strengths, the paH value must be considered a unit on an arbitrary scale.

IV. References

[1] R. G. Bates and S. F. Acree, J. Research NBS **34,** 373 (1945) RP1648.

[2] W. J. Hamer, G. D. Pinching, and S. F. Acree, J. Research NBS **36,** 47 (1946) RP1690.

[3] G. G. Manov, N. J. DeLollis, P. W. Lindvall, and S. F. Acree, J. Research NBS **36,** 543 (1946) RP1721.

[4] S. P. L. Sørensen and K. Linderstrøm-Lang, Compt. rend. trav. lab. Carlsberg **15,** No. 6 (1924).

[5] D. A. MacInnes, Cold Spring Harbor Symposia on Quant. Biol. **1,** 190 (1933).

[6] J. Sendroy, Jr., Trans. Electrochem. Soc. **74,** 595 (1938).

[7] R. G. Bates and S. F. Acree, J. Research NBS **30,** 129 (1943) RP1524.

[8] A. S. Keston, J. Am. Chem. Soc. **57,** 1671 (1935).

[9] R. G. Bates, J. Am. Chem. Soc. **60,** 2983 (1938).

[10] R. G. Bates, G. L. Siegel, and S. F. Acree, J. Research NBS **30,** 347 (1943) RP1537.

[11] H. S. Harned and R. W. Ehlers, J. Am. Chem. Soc. **55,** 2179 (1933).

[12] B. B. Owen and L. Foering, J. Am. Chem. Soc. **58,** 1575 (1936).

[13] B. B. Owen, J. Am. Chem. Soc. **57,** 1526 (1935).

[14] R. K. Gould and W. C. Vosburgh, J. Am. Chem. Soc. **62,** 1817 (1940).

[15] E. Hückel, Physik. Z. **26,** 93 (1925).

[16] E. A. Guggenheim, J. Phys. Chem. **34,** 1758 (1930).

[17] H. S. Harned, A. S. Keston, and J. G. Donelson, J. Am. Chem. Soc. **58,** 989 (1936).

[18] H. S. Harned and R. A. Robinson, Trans. Faraday Soc. **37,** 302 (1941).

[19] H. S. Harned and W. J. Hamer, J. Am. Chem. Soc. **55,** 2194 (1933).

[20] H. S. Harned, J. Am. Chem. Soc. **57,** 1865 (1935).

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Thermal Expansion of Some Copper Alloys

By Peter Hidnert and Harrison S. Krider

This paper gives the results of an investigation on the linear thermal expansion of some brasses, bronzes, and other copper alloys for various temperature ranges between room temperature and 300° C.

The coefficients of expansion of tellurium copper (0.6% of tellurium) are in close agreement with the coefficients of expansion of electrolytic copper (99.97%). The addition of 10 percent of aluminum, 2 percent of iron, and 0.4 percent of tellurium to copper had slight effect on the coefficients of expansion.

Figures 1 and 2 of the paper summarize the coefficients of expansion of copper-zinc alloys and copper-nickel alloys with and without addition of other elements, from the present and previous investigations. The curve for copper-zinc alloys shows that the coefficients of expansion increase with increase in the zinc content. A change in the slope of this curve due to a change from alpha brasses to beta brasses was noted. The addition of 10 to 18 percent of nickel to copper-zinc alloys reduced the coefficients of expansion to a marked extent, but the addition of tin, lead, or aluminum increased the coefficients of expansion.

The curves for copper-nickel alloys in figure 2 indicate that the coefficients of expansion decrease with increase in the nickel content. The curvilinear relation between the coefficients of expansion and nickel content (atomic percent) of copper-nickel alloys is typical of relations for properties of binary alloys having structures composed of solid solutions.

I. Introduction

This paper gives the results of an investigation on the linear thermal expansion of some brasses, bronzes, and copper alloys for various temperature ranges between room temperature and 300° C. One sample of tellurium aluminum bronze was investigated to 400° C.

II. Materials Investigated

The chemical compositions and the treatments of the materials investigated are given in table 1. The samples, the values for chemical compositions, and information about the treatments were furnished by Chase Brass & Copper Co., Waterbury, Conn.

The length of each sample used in the determinations of linear thermal expansion was 300 mm (11.8 in.). The cross sections of the samples were circular, with diameters of 0.20 to 0.37 in. (5 to 9 mm).

III. Apparatus

Two types of precision micrometric thermal-expansion apparatus described by Hidnert [1],[1] and Souder and Hidnert [3] were used for determining the linear thermal expansion of the samples. A stirred liquid bath was used for determinations in the range from 20° to 300° C and an air type heating chamber for determinations in the range from 20° to 400° C.

IV. Results and Discussion

The observations[2] obtained on heating and cooling the samples to various temperatures were plotted. The expansion and contraction curves[2] for all of the samples except 1718 and 1719 showed no irregularities. The expansion curves of samples 1718 and 1719 indicated an irregularity be-

[1] Figures in brackets indicate the literature references at the end of this paper.

[2] Neither the observations nor the curves are presented in this paper.

TABLE 1. *Coefficients of linear expansion of some copper alloys*

Sample	Alloy	Chemical composition [a]									Treatment	Test no. [b]	Average coefficients of expansion per degree centigrade				
		Cu	Ni	Zn	Al	Fe	Te	P	Pb	Other elements			20° to 60° C	20° to 100° C	20° to 200° C	20° to 250° C	20° to 300° C
		Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*			×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶
.....	Electrolytic copper [1]. [c]	99.97	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	[d] 16.6	[d] 16.8	[d] 17.3	.....	[d] 17.7 [e]
1740	Tellurium copper.	99.27	0.01	0.06	.....	0.003	0.65	.....	0.003	.....	Cold drawn and annealed at 1,100° F.	1H	16.8	17.0	17.5	.....	17.9
												1C	.....	17.0	17.4	.....	17.9
1716	Phosnic bronze	98.47	1.19	.....	.....	.....	.....	0.25	.....	.....	Quenched from 1,450° F, age hardened at 850° F for 1 hour, and aged at room temperature for 18 months.	1H	16.5	16.8	17.3	17.5	17.7
												1C	.....	16.8	17.4	.....	17.7
1717	Copper-silicon alloy (Silicon bronze, type B).	97.39	0.04	[f] 1.14	.....	0.02	.....	.....	<0.01	Si 1.41	Annealed at 1,200° F	[g] 1H	16.8	17.1	17.6	.....	18.0
												1C	.....	17.2	17.6	.....	18.1
1718	Tellurium nickel brass [i]	88.84	1.15	[f] 9.28	.....	.....	0.52	0.21	.....	.....	Quenched from 1,450° F, age hardened at 850° F for 1 hour, and aged at room temperature for 19 months.	1H	17.0	17.2	17.6	.....	[h] 17.7
												1C	.....	17.4	17.9	.....	18.4
												2H	17.3	17.4	17.9	18.2	18.4
												2C	.....	17.4	17.9	.....	18.4
1718A	.....do [i]	88.84	1.15	[f] 9.28	.....	.....	.52	.21	.....	.....	Quenched from 1,450° F, age hardened at 850° F for 1 hour, and aged at room temperature for 39 months.	1H	.....	17.2	17.7	18.0	18.2
												1C	.....	.....	.....	.....	18.0
1719	.....do [i]	88.84	1.15	[f] 9.28	.....	.....	.52	.21	.....	.....	Quenched from 1,450° F, cold drawn 34 percent, age hardened at 770° F for 1 hour and aged at room temperature for 18 months.	1H	17.2	17.3	17.7	.....	[h] 17.7
												1C	.....	17.5	17.7	.....	18.1
												2H	17.2	17.4	17.8	18.0	18.1
												2C	.....	17.4	17.8	.....	18.1
1719A	.....do [i]	88.84	1.15	[f] 9.28	.....	.....	.52	.21	.....	.....	Quenched from 1,450° F, cold drawn 34 percent, age hardened at 770° F for 1 hour, and aged at room temperature for 40 months.	1H	17.4	17.5	17.9	18.0	18.2
												1C	.....	17.5	17.8	.....	18.2
1720	Tellurium aluminum bronze.	88.13	.....	.....	[f] 9.50	1.95	.42	.....	.....	.....	Extruded at about 1,550° F and aged at room temperature for 18 months.	1H	16.6	17.0	17.1	.....	17.6
												1C	.....	17.0	17.4	.....	17.8
												2H	16.7	16.9	17.3	.....	17.9
												2C	.....	16.9	17.4	.....	17.9
1720A	.....do.....	88.13	.....	.....	[f] 9.50	1.95	.42	.....	.....	.....	Extruded at about 1,550° F and aged at room temperature for 40 months.	1H	16.4	16.6	17.0	.....	17.8
												1C	16.5	16.8	.....	.....	.....
1721	Aluminum brass.	76.60	.....	[f] 21.47	1.91	0.02	.....	.....	<0.05	.....	Annealed at 1,200° F.	1H	17.8	17.9	18.6	.....	19.5
												1C	.....	18.0	18.5	.....	19.3
1722	Copper (70)-nickel (30) alloy.	[f] 69.42	29.93	0.05	.....	.07	.....	.....	.....	Mn 0.53	Annealed at 1,300° F	1H	15.2	15.4	16.0	.....	16.4
												1C	.....	15.4	15.9	.....	16.5

[a] All compositions in this paper are given in percent by weight except where indicated otherwise.
[b] H indicates heating and C, cooling.
[c] Added for comparison with tellurium copper and the copper alloys in this table.
[d] From Hidnert [1].
[e] From Esser and Eusterbrock [2] for electrolytic copper annealed at 1,020° C.
[f] By difference.
[g] Before this test, sample was heated to 300° C and cooled to room temperature.
[h] Irregularity in expansion curve between 200° and 300° C.
[i] Formerly known as Telnic bronze. All of the zinc has been essentially omitted from Telnic bronze manufactured at the present time.

ween 200° and 300° C during the first heating. However, on repeated heating to 300° C, no irregularities were observed.

Table 1 gives the coefficients of linear thermal expansion that were computed from the curves obtained on heating and on cooling. The coefficients obtained during the first cooling between the maximum temperature and 20° C should apply for repeated heating and cooling through this temperature range.

The maximum difference between the coefficients of expansion of the samples of tellurium copper and Phosnic bronze is 0.3×10^{-6}. The coefficients of expansion of these samples are in close agreement with the coefficients of expansion reported by Hidnert [1] for electrolytic copper, nickeliferous copper (Ni 0.35%) and arsenical copper (As 0.54%).

Nearly all of the coefficients of expansion of the copper-silicon alloy, type B, containing 1.1 percent of zinc and 1.4 percent of silicon, are slightly larger than the coefficients of expansion of tellurium copper.

An examination of the coefficients of expansion of the samples of tellurium nickel brasses and aluminum brass shows that the addition of zinc to copper increased [3] the coefficients of expansion, as was previously shown by Hidnert [1].

The addition of approximately 10 percent of aluminum, 2 percent of iron, and 0.4 percent of tellurium to copper had slight effect on the coefficients of expansion for temperature ranges between 20° and 300° C (see tellurium aluminum bronze). However, an increase of 0.8×10^{-6} was noted for the range from 20° to 400° C.

The addition of 30 percent of nickel and 0.5 percent of manganese to copper decreased the coefficients of expansion by as much as 1.4×10^{-6}.

Figure 1 summarizes coefficients of expansion of copper-zinc alloys with and without additions of other elements, for the range from room temperature (or 0° C) to 300° C, from the present and previous investigations [1, 4, 5, 6, 7]. The curve represents the relation between the coefficients of expansion and the zinc content of the copper-zinc alloys without the addition of other elements in excess of 0.5 percent. This curve shows that the coefficient of expansion increases with increase in the zinc content. The broken portion of the curve indicates a change in slope due to a change from the alpha brasses to beta brasses. The addition of 10 to 18 percent of nickel to copper-zinc alloys reduced the coefficients of expansion to a marked extent, but the addition of tin, lead or aluminum increased the coefficients of expansion. The effect of treatment on some alloys is also indicated in figure 1.

Figure 2 gives a similar summary of the coefficients of expansion of copper-nickel alloys with and without additions of other elements, for several temperature ranges between −183° and +300 ° C, from the present and previous investigations [1, and 6 to 12 inclusive]. The curves represent the relations between the coefficients of expansion and the nickel content of the copper-nickel alloys without the addition of other elements in excess of 0.5 percent. These curves indicate that the coefficients of expansion decrease with increase in the nickel content. The upper curve was drawn as a broken line, for there are not sufficient data available for the binary alloys. The curvilinear relation between the coefficients of expansion and nickel content (atomic percent) of copper-nickel alloys is typical of relations for properties of binary alloys having structures composed of solid solutions.

Data on the linear thermal expansion of other copper alloys investigated at the National Bureau of Standards have been published in previous papers [1, 7, and 13 to 17, inclusive].

[3] Except for the range from 20° to 300° C on samples 1718 and 1719 during the first heating.

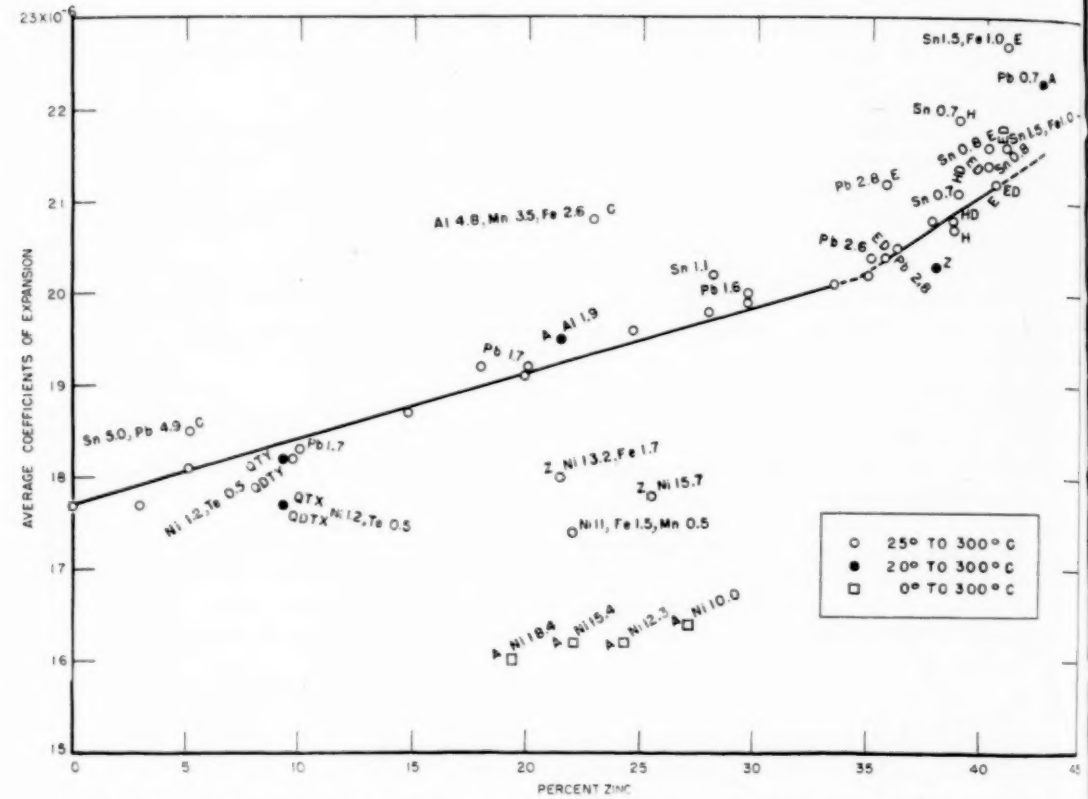

FIGURE 1. *Coefficients of linear expansion of copper-zinc alloys with and without additions of other elements.*

All plotted points represent values for cold-rolled alloys except those marked with one or more of the following symbols: *A*, Annealed; *C*, cast; *D*, drawn; *E*, extruded; *H*, hot-rolled; *Q*, quenched; *T*, tempered; *X*, aged at room temperature about 18 months; *Y*, aged at room temperature about 40 months; and *Z*, unknown treatment.

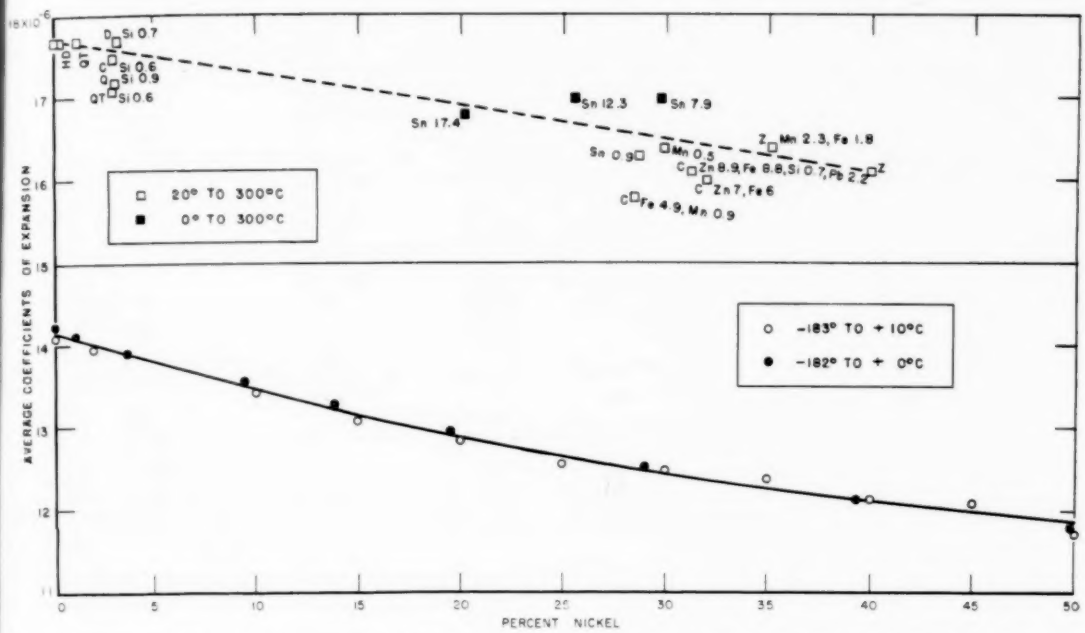

FIGURE 2. *Coefficients of linear expansion of copper-nickel alloys with and without additions of other elements.*

All plotted points represent values for annealed alloys except those marked with one or more of the following symbols: *C*, Cast; *D*, drawn; *E*, extruded; *H*, hot-rolled; *Q*, quenched; *T*, tempered; and *Z*, unknown treatment.

V. References

[1] P. Hidnert, BS Sci. Pap. **17,** 91 (1922) S410.

[2] H. Esser and H. Eusterbrock, Archiv. Eisenhüttenwesen **14,** 341 (1941).

[3] W. Souder and P. Hidnert, BS Sci. Pap. **21,** 1 (1926-27) S524.

[4] Dittenberger and Gehrcke, Z. Instrumentenk. **22,** 112 (1902).

[5] H. von Steinwehr and A. Schulze, Z. Metallkunde **26,** 130 (1934).

[6] M. Cook, J. Inst. Metals **58,** 151 (1936).

[7] P. Hidnert and G. Dickson, J. Research NBS **31,** 77 (1943) RP1550.

[8] L. Holborn and A. Day, Ann. Physik **4,** 104 (1901).

[9] Henning, Z. Instrumentenk. **27,** 115 (1907).

[10] H. Sieglerschmidt, Mitt. Prüfungsamt **38,** 182 (1920).

[11] A. Krupkowski and W. J. De Haas, Communications Phys. Lab. Univ. Leiden **18,** No. 194b (1928) (Translated from Verslag van de Gewone Vergadering der Afdeeling Natuurkunde van de Koninklijke Akademie van Wetenschappen te Amsterdam (27 October 1928), Deel **XXXVII,** 810–818); or A. Krupkowski, Rv. Mét. (Mémoires) **26,** 131, 19 (1929).

[12] S. Aoyama and T. Itô, Sci. Reports Tôhoku Imp. Univ. **27,** 348 (1939).

[13] W. P. Price and P. Davidson, Trans. Am. Inst. Metal **10,** 133 (1916). See appendix (pp. 151 to 164) fo data on thermal expansion by L. W. Schad and P. Hidnert.

[14] P. D. Merica and L. W. Schad, Bul. BS **14,** 571 (191 S321.

[15] P. Hidnert, BS J. Research **12,** 391 (1934) RP665.

[16] P. Hidnert, J. Research NBS **16,** 529 (1936) RP89

[17] P. Hidnert, J. Research NBS **30,** 75 (1943) RP151

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Alkylbenzenes in the C_9 Fraction from Seven Representative Crude Petroleums[1] [2]

By Alphonse F. Forziati [3] and Frederick D. Rossini

This report presents the results of an analysis, by analytical distillation by the A. P. I. Research Project 6, and by spectrographic examination by the Socony-Vacuum Laboratories, the Standard Oil Development Co., and the Sun Oil Co. of the individual C_9 alkylbenzenes (except 1,2,3-trimethylbenzene) and of tertbutylbenzene occurring in the C_9 fraction from the following seven representative crudes: (A) Ponca, Okla.; (B) East Texas; (C) Bradford, Pa.; (D) Greendale-Kawkawlin, Mich.; (E) Winkler, Tex.; (F) Midway, Calif.; (G) Conroe, Tex.

I. Introduction

The previous work of the American Petroleum Institute Research Project 6 on the hydrocarbons in the gasoline fraction of seven representative crudes has been described in three earlier reports of investigations [1, 2, 3] *

At the time of the last report, the status of the work was as follows:

(a) Each of the seven naphthas had been separated by adsorption into an aromatic portion and a paraffin-naphthene portion.

(b) Each paraffin-naphthene portion and each aromatic portion had been separately distilled analytically.

(c) For the paraffin-naphthene portion, the analysis of the individual components normally boiling below 102° C had been completed, and, in addition, the amounts of *n*-octane and *n*-nonane had been evaluated. The analysis of the paraffins and naphthenes normally boiling in the range 102° to 180° C was in process.

(d) For the aromatic portion, the analysis of the individual components normally boiling below 160° C has been completed.

Although the eight possible aromatic hydrocarbons whose normal boiling points are below 160° C were relatively easily determined (from measurements of boiling points, refractive indices, and freezing points), the twelve possible aromatic hydrocarbons in the range 160° to 180° C are present in such relatively smaller amounts, and with such small differences in boiling point, that it is possible to obtain from the boiling point-volume curves (on the limited quantity of material processed) only values for close-boiling mixtures (usually pairs). Further, the lack of adequate amounts of nearly pure stocks of each of the component hydrocarbons made it impossible to utilize the method of determining individual hydrocarbons in mixtures of hydrocarbons by measuring freezing points [4,5].

As purified samples of these alkylbenzenes were becoming available for spectrometer calibration, it is was evident that the analysis of the individual aromatic hydrocarbons in the material normally boiling above 160° C could be performed successfully by spectrographic methods. Accordingly, with the approval of the Advisory Committee for the American Petroleum Institute Research Project 6, the cooperation of three laboratories that had experience in the spectrographic analysis of the C_9 alkylbenzenes was enlisted. These laboratories were those of the Socony-Vacuum Oil Co., Paulsboro, N. J., the

[1] This investigation was performed as part of the work of the American Petroleum Institute Research Project 6 on the "Analysis, Purification, and Properties of Hydrocarbons" at the National Bureau of Standards.

[2] Presented before the Division of Petroleum Chemistry of the American Chemical Society at Atlantic City, N. J., April, 1947.

[3] Research Associate on the American Petroleum Institute Research Project 6.

* Figures in brackets indicate the literature references at the end of this paper.

Standard Oil Development Co., Elizabeth, N. J., and the Sun Oil Co., Norwood, Pa. The Socony-Vacuum and Standard Oil Development Laboratories agreed to make infrared and the Sun Oil Laboratory, Raman spectral measurements.

II. Material Analyzed

The seven naphthas under investigation, which have been described in detail in the previous reports [1, 2, 3], are the following: A, Ponca, Okla.; B, East Texas; C, Bradford, Pa.; Greendale-Kawkawlin, Mich.; E, Winkler, Tex.; F, Midway, Calif.; G, Conroe, Tex.

The aromatic portions, boiling between 148° and 180° C, from each of the seven naphthas, were blended,[4] into five lots, as shown in fig 1 to 7, inclusive, which give the temperat volume curves from the original analytical di lations of these materials, as previously give the second published report[5] of this work [2].

[4] Although two of the cooperating laboratories preferred to have the ing for spectrographic analysis made from "flat to flat" rather than "break to break," the material had previously been blended in the way for five of the naphthas in order to reduce losses by evaporatio therefore, the blending for the remaining two naphthas was also mad "break to break." This made the spectrographic analyses more diffic those laboratories whose normal operating procedures were based on bl from "flat to flat."

[5] The figures 8 to 14 in the previously published report give, except Bradford (Pa.) and Winkler (Tex.) naphthas, a plot of refractive against volume. The aromatic portions of five of the naphthas, (Okla.), East Texas, Greendale-Kawkawlin (Mich.), Midway (Calif. Conroe (Tex.), are seen to be substantially 100 percent aromatic, by parison of the values of refractive index of the aromatic distillate and pure components (indicated by crosses at the appropriate places).

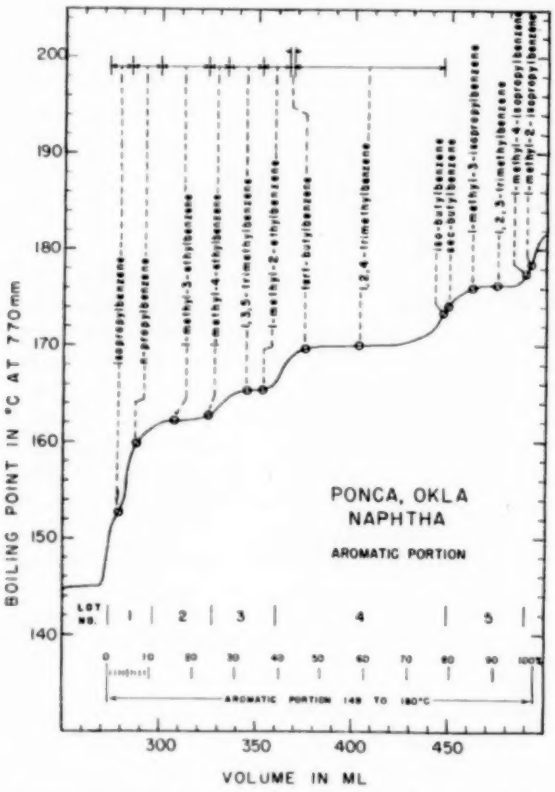

FIGURE 1. *Plot of the boiling point as a function of the volume for the C_9 fraction of the aromatic portion of the Ponca, Okla., naphtha.*

The lot numbers refer to the portions of the distillate reblended for spectrographic examination.

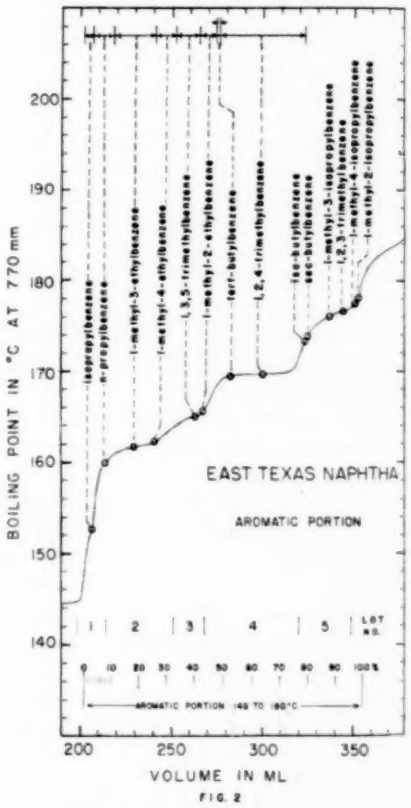

FIG. 2

FIGURE 2. *Plot of the boiling point as a function of volume for the C_9 fraction of the aromatic portion of East Texas naphtha.*

The lot numbers refer to the portions of the distillate reblended for spectrographic examination.

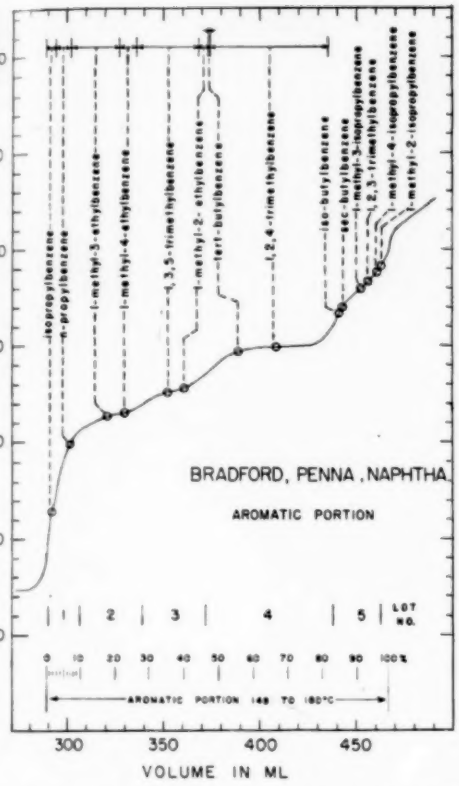

FIGURE 3. *Plot of the boiling point as a function of the volume for the C_9 fraction of the aromatic portion of the Bradford, Pa., naphtha.*

The lot numbers refer to the portions of the distillate reblended for spectrographic examination.

At that time, the refractive index-volume plots for the aromatic portion of the Bradford (Pa.) and Winkler (Tex.) naphthas were not shown because the refractive index fell somewhat below the proper values for the aromatic components. Calculations made on the basis of the refractive index expected for 100 percent aromatic material, yielded the following values for the percentage of paraffin-naphthene material remaining in lots 1 to 5:

Bradford (Pa.), naphtha: lot 1, 21 percent; lot 2, 5 percent; lot 3, 5 percent; lot 4, 4 percent; lot 5, 5 percent.

Winkler (Tex.), naphtha: lot 1, 14 percent; lot 2, 3 percent; lot 3, 3 percent; lot 4, 8 percent; lot 5, 14 percent.

For spectrographic examination by the cooperating laboratories, the following samples were prepared and transmitted:

To the Socony-Vacuum Oil Co. and Standard Oil Development Co., for infrared analysis: Samples (4 to 5 ml) of each of the five lots (1 to 5) of each of the seven naphthas.

To the Sun Oil Co., for Raman analysis: Samples (7 to 8 ml) of lot 3 of the East Texas naphtha, and lot 1 of the Bradford, Pa., Greendale-Kawkawlin, Mich., and Midway, Calif., naphthas; Samples (13 to 15 ml) of each of the remaining lots, except lot 1 of East Texas and Conroe, Tex., naphthas.

As the pure hydrocarbons representing the expected components of lot 5 were at that time not yet available for calibrating spectrometers,

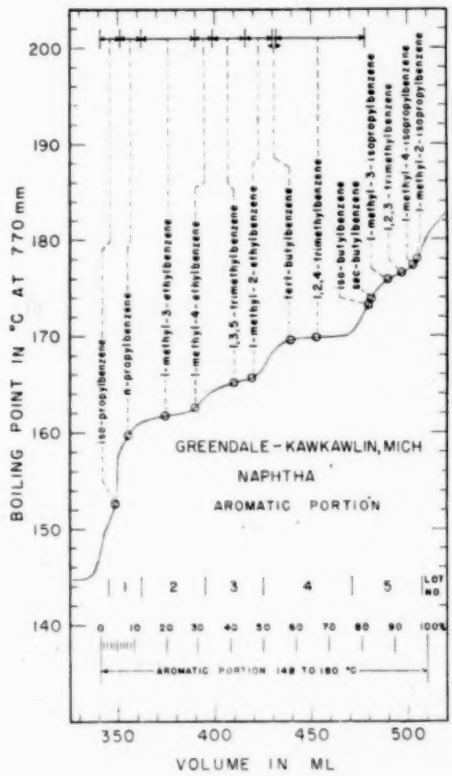

FIGURE 4. *Plot of the boiling point as a function of the volume for the C_9 fraction of the aromatic portion of the Greendale-Kawkawlin, Mich., naphtha.*

The lot numbers refer to the portions of the distillate reblended for spectrographic examination.

the cooperating laboratories were requested to report only on lots 1, 2, 3, and 4.

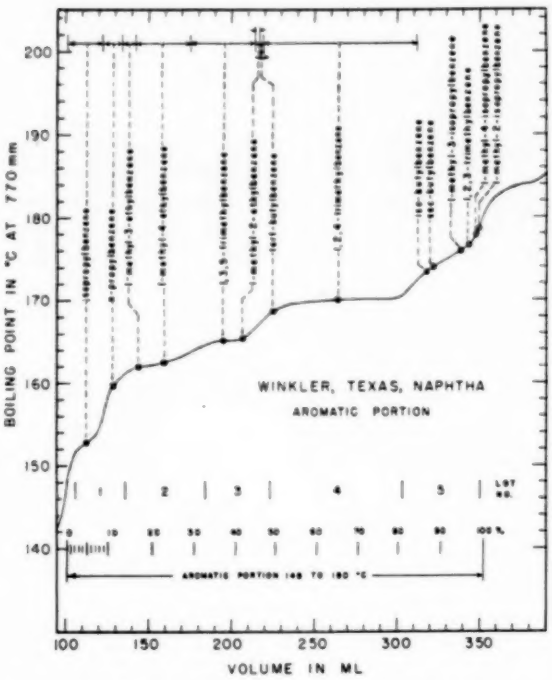

FIGURE 5. *Plot of the boiling point as a function of the volume for the C_9 fraction of the aromatic portion of the Winkler, Tex., naphtha.*

The lot numbers refer to the portions of the distillate reblended for spectrographic examination.

III. Data of the Cooperating Laboratories

The spectrographic data from the laboratories of the Socony Vacuum Oil Co., Standard Oil Development Co., and Sun Oil Co., are given in table 1. The data from the analytical distillations, by the API Research Project 6, of the aromatic portion of the seven naphthas (shown in figures 1 to 7) yielded values (given in table 2) for the amounts of the following components or pairs of components: isopropylbenzene; *n*-propylbenzene; 1-methyl-3-ethylbenzene plus 1-methyl-4-ethylbenzene; 1,3,5-trimethylbenzene plus 1-methyl-2-ethylbenzene; tert-butylbenzene plus 1,2,4-trimethylbenzene.

IV. Evaluation of the Data

From the values reported by the three laboratories on the spectrographic analysis of the several lots of the seven naphthas, the total amount of each component found by a given laboratory in all four lots (1 to 4) was computed. These values, given for each component for each naphtha analyzed, and expressed as a percentage by volume of the aromatic portion 148° to 180° C, are given in columns 2, 3, and 4 of table 2. In the case of the East Texas, Bradford (Pa.), and Conroe (Tex.) naphthas, the values for 1-methyl-3-ethylbenzene from the Sun Oil Co. were increased as shown, the increase being simply the average of the amounts of this component found by the Socony-Vacuum and Standard Oil Development

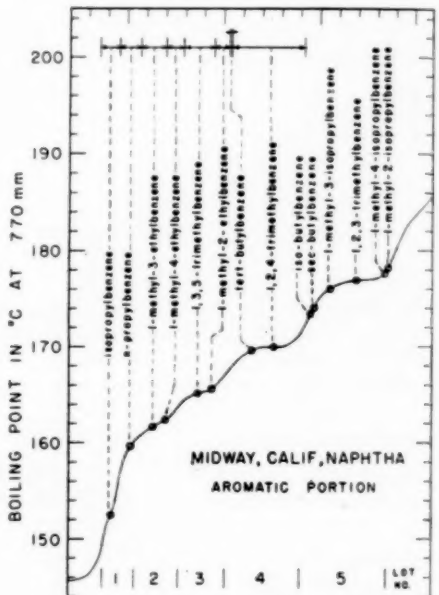

FIGURE 6. *Plot of the boiling point as a function of the volume for the C_9 fraction of the aromatic portion of the Midway, Calif., naphtha.*

The lot numbers refer to the portions of the distillate reblended for spectrographic examination.

TABLE 1. *The amounts of the individual hydrocarbons in lots 1 to 4 of the C_9 aromatic portion of the seven representative naphthas, as determined spectrographically by the three laboratories*

Lot number and hydrocarbons	Naphtha (see text)																				
	A			B			C			D			E			F			G		
	Laboratory[b]																				
	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
	Percentage by volume of the given lot																				
Lot 1																					
o-xylene	3	9	12	3	14	–	3	13	–	3	8	9.5	0	2	0	6	18	16.5	6	16	–
isopropylbenzene	27	42	25	27	41	–	12	18	–	12	29	14	49	62	55.5	38	51	39.5	14	23	–
n-propylbenzene	60	45	48.5	59	34	–	47	18	–	57	41	44	45	14	18	50	28	33	45	32	–
1-methyl-3-ethylbenzene	10	2	14.5	11	8	–	38	13	–	28	17	27.5	4	7	11.5	6	0	11	35	23	–
1-methyl-4-ethylbenzene	0	2	0	0	3	–	0	4	–	0	5	5	2	15	15	0	3	0	0	6	–
Lot 2																					
isopropylbenzene	0	1	–	0	0	–	0	0	–	0	3	–	0	0	–	0	2	–	0	0	–
n-propylbenzene	16	10	13	16	10	10.5	12	3	9.5	16	9	10.5	14	0	–	21	25	–	15	8	7
1-methyl-3-ethylbenzene	67.7	62	64.5	56	54	56	61	44	54	64	54	66	15	10	–	54	35	–	60	55	64.5
1-methyl-4-ethylbenzene	16	22	21.5	19	26	26.5	15	19	20.5	16	22	20	55	60	–	18	22	–	15	23	18
1,3,5-trimethylbenzene	0.3	3	1	6	6	7	10	17	16	3	3	3.5	15	21	–	5	8	–	8	11	10.5
1-methyl-2-ethylbenzene	0	2	0	3	4	0	2	3	0	1	0	0	1	1	–	2	1	–	2	3	0
tert-butylbenzene	–	0	–	–	0	–	–	0	–	–	0	–	–	1	–	–	0	–	–	0	–
1,2,4-trimethylbenzene	–	0	–	–	0	–	–	0	–	–	0	–	–	7	–	–	0	–	–	0	–
Lot 3																					
1-methyl-3-ethylbenzene	9	11	8	9	9	9.5	5	8	7	9	11	8	0	1	–	11	10	10	5	4	7.5
1-methyl-4-ethylbenzene	8	9	9.5	8	8	9.5	3	7	9.5	8	9	11.5	2	8	–	12	13	15.5	3	6	6
1,3,5-trimethylbenzene	46	41	42.5	50	45	41.5	71	65	65	49	41	40	78	64	–	49	39	36.5	60	45	49
1-methyl-2-ethylbenzene	28	30	33	27	33	37.5	9	12	12.5	28	33	37.5	4	8	–	21	28	32.5	10	17	11.5
tert-butylbenzene	0	4	0	0	3	0	0	1	0	0	3	0	0	3	–	0	4	0	0	3	0
1,2,4-trimethylbenzene	9	5	7	6	2	2	12	7	6	6	3	3	16	16	–	7	6	5.5	22	25	26
Lot 4																					
1-methyl-4-ethylbenzene	–	0	–	–	0	–	–	0	–	–	0	–	–	0	–	–	4	–	–	0	–
1,3,5-trimethylbenzene	4	5	2.5	6	5	5	10	11	8	5	6	4	4	5	–	9	9	5	2	0	1
1-methyl-2-ethylbenzene	3	8	5.5	4	9	5	2	2	0	4	9	7	0.5	2	–	4	6	6.5	0.5	2	0
tert-butylbenzene	0.7	1	2.5	0.5	1	3	0	1	0	0	2	2.5	1	1	–	0.7	1	0	0.5	2	2
1,2,4-trimethylbenzene	83.5	76	88.5	85	74	86	83.2	72	92	90	71	86.5	93.5	74	–	83.5	69	87	90.7	77	96
Iso-butylbenzene	0	a	0	0	a	0	0	a	0	0	a	0	0	a	–	0	a	0	0	a	0
1,2,3-trimethylbenzene	0.8	a	1	0.5	a	1	0.8	a	0	0	a	0	0	a	–	0.8	a	1.5	0.8	a	1

[a] Values determined but not reported.

[b] The Roman numerals identify the following laboratories and methods used: I, Socony-Vacuum Oil Co., infrared; II, Standard Oil Development Co., infrared; III, Sun Oil Co., Raman.

TABLE 2. *Results of the analyses of the C_9 alkylbenzenes (except 1,2,3-trimethylbenzene) and tert-butylbenzene in the seven naphthas*

| Hydrocarbon | Analysis | | |

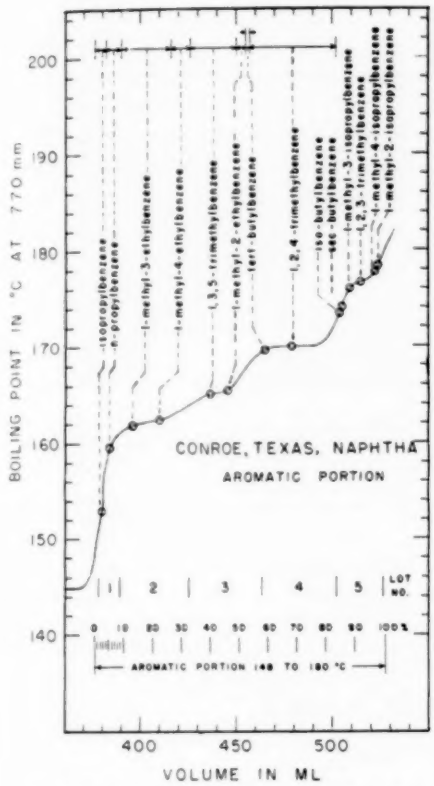

FIGURE 7. *Plot of the boiling point as a function of the volume for the C_9 fraction of the aromatic portion of the Conroe, Tex., naphtha.*

The lot numbers refer to the portions of the distillate reblended for spectrographic examination.

laboratories in lot 1, which, for these naphthas, was not analyzed by the Sun Oil laboratory. Uniformly for the spectrographic values from all three laboratories, the amount of 1,2,4-trimethylbenzene was increased by the amount indicated, in order to account for the amount of this component expected to be in lot 5, which has not yet been analyzed spectrographically. The amount to be added was deduced from a correlation of the value for the amount of tert-butylbenzene plus 1,2,4-trimethylbenzene reported by the API Research Project 6, which includes the amount of this component in lot 5, with the boiling point at the end of lot 4, for each naphtha. This correction to the amount of 1,2,4-trimethylbenzene is smallest (1.2%) for the Ponca (Okla.) naphtha and largest (7.2%) for the Winkler (Tex.) naphtha, which is in accord with the fact that the boiling point at the end of lot 4 is highest for the Ponca (Okla.) naphtha and lowest for the Winkler (Tex.) naphtha.

The values from the boiling point-volume data of the API Research Project 6 are given in column 5 of table 2.

The values given in the last column of table 2, representing the final selected "best" values for the amount of each of the given components in each naphtha, were obtained in the following way:

(a) The amount of isopropylbenzene was taken to be that given by the data of the API Research Project 6. (A more accurate value for isopropylbenzene could have been obtained from the spectrographic data if the material just preceding lot 1 could have been examined spectrographically, so that spectrographic values for the total amount of this component would have been available.)

(b) The amount of *n*-propylbenzene was taken as the average of the values from the four (or three) laboratories, as given.

(c) The sum of the amounts of 1-methyl-3-ethylbenzene and 1-methyl-4-ethylbenzene was taken as the average of the values from the four (or three) laboratories, as given. The relative amounts of the two components was taken as the average of the relative amounts given by the spectrographic analyses.

(d) The final values for 1,3,5-trimethylbenzene and 1-methyl-2-ethylbenzene were obtained in a manner exactly analogous to the procedure described for 1-methyl-3-ethylbenzene and 1-methyl-4-ethylbenzene.

(e) The final values for tert-butylbenzene and 1,2,4-trimethylbenzene were obtained in the same manner as the preceding pair.

V. Summary of the Results

Table 3 gives, for the seven naphthas, the amounts of the C_9 alkylbenzenes (except 1,2,3-trimethylbenzene) and tert-butylbenzene, expressed as a percentage by volume of (a) the total aromatics to 180° C; (b) the naphtha 40° to 180° C; (c) the crude petroleum.

Table 4 gives the relative amounts of the C_9 alkylbenzenes (except 1,2,3-trimethylbenzene) and tert-butylbenzene in the seven representative naphthas.

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TABLE 3. *Summary of the amounts of the C_9 alkylbenzenes (except 1,2,3-trimethylbenzene) and tert-butylbenzene in the seven naphthas*

Hydrocarbon	Amount of the given hydrocarbon expressed as percentage by volume of																				
	Total aromatics to 180°C.							Naphtha 40° to 180°C.							Crude Petroleum						
	A	B	C	D	E	F	G	A	B	C	D	E	F	G	A	B	C	D	E	F	G
isopropylbenzene	2.2	1.4	1.1	2.0	6.0	3.0	1.2	0.22	0.12	0.11	0.13	0.22	0.19	0.33	0.07	0.04	0.03	0.03	0.03	0.03	0.09
n-propylbenzene	3.0	3.2	1.8	2.2	3.5	3.2	1.6	0.29	0.28	0.18	0.15	0.13	0.21	0.46	0.09	0.08	0.05	0.03	0.02	0.04	0.12
1-methyl-3-ethylbenzene	5.2	6.5	5.2	5.4	2.3	3.9	5.0	0.51	0.57	0.52	0.37	0.08	0.25	1.47	0.17	0.16	0.13	0.08	0.01	0.04	0.40
1-methyl-4-ethylbenzene	1.9	2.9	1.9	1.9	9.2	2.6	1.7	0.19	0.26	0.19	0.13	0.34	0.17	0.49	0.06	0.07	0.05	0.03	0.05	0.03	0.13
1,3,5-trimethylbenzene	3.6	3.7	6.8	3.2	11.0	4.8	4.6	0.35	0.32	0.68	0.22	0.40	0.31	1.34	0.12	0.09	0.17	0.05	0.05	0.05	0.36
1-methyl-2-ethylbenzene	3.0	2.7	1.0	2.6	1.1	2.6	1.1	0.29	0.24	0.10	0.18	0.04	0.17	0.32	0.09	0.07	0.03	0.04	0.01	0.03	0.09
tert-butylbenzene	0.4	0.3	0.1	0.2	0.4	0.2	0.2	0.03	0.02	0.01	0.01	0.02	0.02	0.05	0.01	0.01	0.00	0.00	0.00	0.00	0.01
1,2,4-trimethylbenzene	15.8	13.4	13.2	9.3	26.5	11.2	8.8	1.53	1.18	1.31	0.64	0.97	0.72	2.56	0.51	0.34	0.33	0.15	0.13	0.13	0.69

TABLE 4. *Relative amounts of the C_9 alkylbenzenes (except 1,2,3-trimethylbenzene) and tert-butylbenzene in seven representative naphthas*

Compound	Naphtha (See text)							Range of values	Average value
	A	B	C	D	E	F	G		
	Relative amounts								
Isopropylbenzene	6.4	4.2	3.4	7.3	10.0	9.5	4.8	3 to 10	7
n-Propylbenzene	8.4	9.5	5.9	8.1	5.8	10.3	6.5	6 to 10	8
1-Methyl-3-ethylbenzene	15.0	19.0	16.8	20.2	3.8	12.4	21.0	[a] 4 to 21	15
1-Methyl-4-ethylbenzene	5.5	8.6	6.1	7.3	15.3	8.1	6.9	6 to [b] 15	8
1,3,5-Trimethylbenzene	10.2	10.7	22.0	12.1	18.4	15.3	19.1	10 to 22	15
1-Methyl-2-ethylbenzene	8.5	8.0	3.3	9.6	1.8	8.1	4.5	2 to 10	6
tert-Butylbenzene	1.0	0.8	0.2	0.7	0.7	0.7	0.7	0 to 1	1
1,2,4-Trimethylbenzene	45.0	39.2	42.3	34.7	44.2	35.6	36.5	35 to 45	40
Total	100	100	100	100	100	100	100	.....	100

[a] Excluding naphtha E, the lower limit here would be 12 instead of 4.
[b] Excluding naphtha E, the upper limit here would be 9 instead of 15.

The results of the present investigation indicate that the alkylbenzenes in the C_9 fraction of petroleum are present in relative amounts that are of the same magnitude for different crude petroleums, with the exception that in the Winkler, Tex., naphtha, E, the 1-methyl-3-ethylbenzene and the 1-methyl-4-ethylbenzene are reversed from the usual order. The range and average values are given in the last column of table 4. This follows similar relations previously reported for the lower alkylbenzenes and for certain other groups of hydrocarbons in different crudes.

Although the connection is not apparent at this writing the average relative amounts of the five polyalkylbenzenes listed in table 4, representing the average relative occurrence of these compounds in the liquid state in these petroleums, are remarkably close to the relative amounts of these five compounds that would be present at thermodynamic equilibrium in the gas phase at 400°C as calculated from recently published thermodynamic

data for these compounds [6]. The relative amounts of these five polyalkylbenzenes are as follows, for the liquid state in these natural petroleums, on the average, and for thermodynamic equilibrium in the gas phase at 400°C, respectively: 1-methyl-2-ethylbenzene, 7, 6; 1-methyl-3-ethylbenzene, 18, 17; 1-methyl-4-ethylbenzene, 9, 11; 1,2,4-trimethylbenzene; 48, 48; 1,3,5-trimethylbenzene, 18, 18. The relative amounts of the two propylbenzenes do not, however, show any accord with the foregoing.

Information regarding the spectrographic apparatus and procedure used by the laboratories of the Socony-Vacuum Oil Co., the Standard Oil Development Co., and the Sun Oil Co. in the spectrographic analyses reported here may be obtained directly from those laboratories.

The American Petroleum Institute Research Project 6 is indebted to the Socony-Vacuum Oil Co., the Standard Oil Development Co., and the Sun Oil Co. for the participation of their research laboratories in the spectrographic analyses of the C_9 aromatic fractions described in this report. The spectrographic analyses were made possible by the following persons to whom grateful acknowledgment is hereby made: Socony-Vacuum Oil Co., Paulsboro, N. J.: P. V. Keyser, Jr., C. H. Schlesman, E. T. Scafe, and F. P. Hochgesang; Standard Oil Development Co., Elizabeth, N. J.: W. J. Sweeney, E. D. Reeves, S. C. Fulton, H. J. Hall; Sun Oil Co., Norwood, Pa.: J. Bennett Hill, S. S. Kurtz, Jr., E. J. Rosenbaum.

VI. References

[1] F. D. Rossini, B. J. Mair, A. F. Forziati, A. R. Glasgow, Jr., and C. B. Willingham, Proc. Am. Petroleum Inst. **23, III**, 7 (1942); Oil Gas J. **41,** No. 27, 106 (1942); Petroleum Refiner **21,** No. 11, 73 (1942).

[2] A. F. Forziati, C. B. Willingham, B. J. Mair, and F. D. Rossini, Proc. Am. Petroleum Inst. **24, III,** 34 (1943); Petroleum Refiner **23,** No. 11, 109 (1943); J. Research NBS **32,** 11 (1944) RP 1571.

[3] A. F. Forziati and F. D. Rossini, "Some additional data on the gasoline fraction of seven representative crudes." American Petroleum Institute Research Project 6, National Bureau of Standards. (Report issued May 6, 1944.)

[4] A. J. Streiff and F. D. Rossini. J. Research NBS **32,** 185 (1944) RP1584.

[5] A. J. Streiff and F. D. Rossini, J. Research NBS **39,** 331 (1947) RP1833.

[6] W. J. Taylor, D. D. Wagman, M. G. Williams, K. S. Pitzer, and F. D. Rossini, J. Research NBS **37,** 95 (1946) RP1732.

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Experimental Study of the Koppers-Hinckley-Podbielniak Apparatus and Method for the Determination of Conjugated Dienes

By Martin Shepherd, Richard Thomas, Shuford Schuhmann, and Vernon Dibeler

There is reported an experimental study of the accuracy, reproducibility, and general operating characteristics of the Koppers-Hinckley-Podbielniak apparatus and Analytical Method L. M. 2.1.1.7 (or 2.1.1.9) of the Office of Rubber Reserve for the determination of conjugated dienes in hydrocarbon mixtures. Physical equilibria and physico-chemical behavior of the analytical system are discussed, accuracy and reproducibility are evaluated, and certain operating precautions are given.

I. INTRODUCTION

The experimental study of the Koppers-Hinckley-Podbielniak apparatus and Analytical Method L. M. 2.1.1.7 (or 2.1.1.9) of the Office of Rubber Reserve (hereinafter designated RuR) was conducted early in 1945, and most of the information obtained was submitted for discussion on February 15 and 16, 1945, at Meeting No. 9 of the Committee on Butadiene Specification and Methods of Analysis, Office of Rubber Reserve, and released in the minutes of that meeting, pages 23 to 48.

Since this time additional information has been obtained, and a practical estimation of the usefulness of the apparatus and the degree of reliability of the method has been made. This estimation is given essentially in the condensed conclusions, placed ahead of the account of the experiments to serve readers whose time and interest may be limited.

The original and the additional observations are collected here for the convenient reference of those who use this apparatus and method, or depend upon its results. The method itself was designed for the determination of 1–3 butadiene in specification grades of this substance used for the manufacturing of synthetic rubber. It is based upon the rapid and quantitative absorption of conjugated dienes in molten maleic anhydride at approximately 100° C. The other constituents of the sample that dissolve abundantly in the maleic reagent are freed from physical solution by displacement with a stream of air-free carbon dioxide. The volumes of the initial sample and of the residue are compared to establish the total impurity, and the balance is reported as conjugated dienes, or, if knowledge of the sample permits, as 1–3 butadiene.

II. Condensed Conclusions

The practical conclusion reached after an experimental study of the Koppers-Hinckley-Podbielniak apparatus and RuR method L. M. 2.1.1.7 (or 2.1.1.9) is essentially this: The apparatus and method give satisfactory results for the determination of 1,3-butadiene in specification-grade butadiene, but results obtained with mixtures of lesser purity are not always satisfactory.

This conclusion may be further qualified by stating the obvious fact that the determination of 1,3-butadiene will not be satisfactory in the case of mixtures containing significant amounts of C_5 or C_8 hydrocarbons until an adequate method for the determination and possibly the removal of the interfering compounds has been developed. Only then can a satisfactory correction be made for their presence, and without this correction the determination of butadiene carries with it the

uncertainty attached to the determination of the interfering heavier compounds.

The conclusion stated in the first paragraph is in no disagreement with the claims of Hinckley, who has repeatedly stated that the apparatus was intended for the determination of conjugated dienes in specification-grade butadiene. The application of the apparatus and method to mixtures of lesser purity was obviously intended by the Office of Rubber Reserve, however, since the burette supplied is capable of measuring 110 percent of impurity in the sample, and the stated scope of the method RuR (L. M. 2.1.1.7 or L. M. 2. 1.1.9), includes "recycle-grade butadiene" and "butadiene in any concentration in C_4 and lighter mixtures." The desire to extend the scope of the method to samples of purity less than specification grade has complicated the analytical picture, and the extent of this complication may be about as follows:

1. In the approximate range 95 to 85 percent butadiene, reproducibilities ranging from ± 0.01 to ± 0.4 percent of the whole sample have been observed under prescribed operating conditions. Larger variations have occasionally been observed. In this range agreement with the mass spectrometer may be as good as ± 0.2 to ± 0.4 percent, but greater variance has been observed.

2. In the approximate range 15 to 2 percent butadiene, reproducibilities of about ± 0.4 percent may be expected, but wider variations have been observed. Agreement within 2.0 percent of results obtained by the mass spectrometer may be expected.

From the practical viewpoint, these conclusions are important:

1. Several determinations of conjugated dienes in every sample must be made in order to establish the proper behavior of the apparatus with respect to reproducibility.

2. Samples of different composition cannot be run successively through the apparatus without upsetting equilibrium in the maleic absorber to an extent so great that the time lost in establishing the required new equilibrium is excessive. In the end, efficient operation of the analytical laboratory demands one apparatus for each kind of sample analyzed.

3. The Koppers-Hinckley-Podbielniak apparatus examined presented a serious health hazard by liberating harmful amounts of mercury vapor into the laboratory air. (The design has recently been modified in the attempt to eliminate this hazard.*)

III. General Plan of Experimental Study

The general physico-chemical behavior of the absorption system was studied principally by means of analyses of inlet and outlet gases. These analyses were made by the mass spectrometer. For each of several mixtures of different compositions, reproducibility was measured in such a way that any change of composition on sampling was eliminated from the measurement. Accuracy was estimated by comparison with the mass spectrometer and the freezing point method.

Several modifications of the maleic reagent were studied. The effects of rate of flow, composition of reagent, and change of composition of samples were observed. General operating characteristics were noted, and some suggestions for modification of apparatus and procedure were derived.

IV. Physical Equilibria in the Koppers-Hinckley Apparatus

In the volumetric determination of conjugated dienes by reaction with maleic anhydride or similar reagents, large errors may be caused by the solution of various constituents of the gas sample, which do not themselves react. The essential feature of the Hinckley apparatus is the provision for displacing dissolved gases from the reagent used to remove conjugated dienes. This displacement is effected by a stream of carbon dioxide (sufficiently air-free), which delivers the portion of the sample that does not react through a strong solution of potassium hydroxide to a burette where

* This report was prepared late in 1945. Since its preparation there have been advanced two variations of the methods here cited. One of these is the Shell-Torrance Modification that employs a second buret for the measurement of residue, as suggested in this report. The other modification is number 10 in the progression of the RuR L. M. 2.1.1.—Series. L. M. 2.1.1.10 employs a modified CO_2 absorber and notes two changes of procedure: (1) Excess stopcock lubricant is removed by a benzene flush; (2) 40 ml of fresh KOH is introduced at the top of the buret for measuring residues at the beginning of each analysis. Hinckley has offered a few observations to indicate that these changes have made it possible to attain a reproducibility of ± 0.2 percent instead of the ± 0.4 percent noted above. However, no such claim is made in the description of either of the two newer modifications of L. M. 2.1.1.7 or L. M. 2.1.1.9. There is no change of sufficient significance in the modified physical-chemical picture offered by L. M. 2.1.1.10 to tempt the prediction that a reproducibility of ± 0.2 percent would be generally realized in the alternate analysis of samples of widely varying composition, without equilibration between analyses. Of the two modifications, that advanced by Shell-Torrance is based on sounder physical principles in regard to eliminating the error of a shifting saturation pressure with respect to water vapor in the residue, a matter discussed in the body of the present report.

is collected over the solution of potassium hydroxide.

The equilibria with respect to dissolved gases within this apparatus are accordingly pertinent aside from the chemical reaction, since they considerably determine not only the degree of accuracy achieved but also directly set the operating requirements with respect to obtaining necessary blanks—a very practical consideration from the viewpoint of total time required. Approximately, the following physical picture may be expected within the apparatus:

1. A fresh dose of maleic anhydride and a new charge of potassium hydroxide solution are poured into their allotted compartments. Carbon dioxide is then put through the apparatus until the entrained air is almost completely displaced and the residue shows an accumulation of gas over the potassium hydroxide no greater than 0.01 ml per 30 minutes. At this time the condition of the two reagents is about as follows:

(a) The maleic anhydride is approximately saturated with respect to carbon dioxide and probably contains very little dissolved air.

(b) The potassium hydroxide solution contains dissolved air, which has not been displaced by the carbon dioxide. (Even when pure carbon dioxide is absorbed by a solution of potassium hydroxide, a residual minute bubble always remains following the complete absorption of CO_2, providing the solution contains any dissolved air, which it always does unless the air has been carefully removed. This occurs because air is displaced to the gas phase during the absorption and eventual disappearance of the bubbles of CO_2.)

2. Next a measured sample of the hydrocarbon mixture is pushed through the maleic anhydride by the continued stream of carbon dioxide, and the unreacted residue is in turn pushed through the CO_2 absorber and collected over the potassium hydroxide in the burette. The residue is collected until its volume remains constant, which is the moment designated for its measurement. At this time, the condition of the two reagents is about as follows:

(a) The maleic anhydride contains some dissolved hydrocarbons that have not yet been completely displaced by the carbon dioxide, and the residue is correspondigly too small.

(b) The potassium hydroxide contains dissolved hydrocarbons, which in turn have displaced some air to the collected residue. Since the hydrocarbons are more soluble than air, the residue is too small by this difference. The potassium hydroxide is not yet in equilibrium with the hydrocarbons delivered as residue.

(c) The potassium hydroxide is mixed with potassium carbonate, and the solution now has a different vapor pressure.

These conditions, given in (2a) and (2b) above, have been illustrated experimentally:

(2a) The presence of dissolved hydrocarbons in the maleic anhydride was shown as follows:

After 11 analyses of a sample containing about 15 percent of 1,3-butadiene, a blank was obtained by purging with CO_2. This required about 7 hours. At the end of 3½ hours, 0.75 ml of residue had been collected. The analysis of this residue by mass spectrometer was:

	Percent
Propadiene	1. 2
Propane	7. 8
1, 3-Butadiene	1. 2
1-Butene	39. 6
2-Butene	39. 3
Iso-butane	0. 8
n-Butane	8. 9
Pentenes	1. 1
Vinyl cyclohexene	0. 1

(2b) The fact that the potassium hydroxide solution dissolves notable amounts of the hydrocarbons composing the residue may be shown by collecting the residue and reading the volume with lapsing time. Here is an example:

Time	Volume of residue
	ml
2:39 p. m.	0. 00
2:54	3. 65
2:55	3. 64
2:56	2. 63
2:58	2. 62
3:00	3. 60
3:02	3. 57
3:04	3. 55
3:06	3. 52
3:09	3. 51
8:30 a. m. (following day)	3. 34

This overnight reduction of volume is always noted. The immediate contraction after obtaining an apparent maximum is not always noted, but for the sake of reproducibility (and greater

approach to accuracy) it appears important to capture the reading at its maximum.

The condition given in (2c) above introduces another error. The continual conversion of the potassium hydroxide to the carbonate, with a consequent increase of the saturation pressure of the solution, imposes the condition that no two gas volumes taken successively are comparable with respect to the pressure of water vapor. The measurement of the residue is converted (by means of a chart) for the change of the saturation pressure of the solution of potassium hydroxide with changing temperature; but this measurement still remains in error by an amount corresponding to the difference between the saturation pressure of the hydroxide and that of the varying mixtures of hydroxide and carbonate over which the residue is collected. This may amount to as much as 2 percent, depending upon volume of residue, concentration of carbonate, and temperature. The error may be corrected if the saturation pressures are known, but such a correction involves knowledge of the composition of the solution as well as the temperature. A similar case was studied in the Van Slyke Manometric Apparatus.[1]

Such an error is easily eliminated by designing the apparatus to permit measurement of the volumes to be compared in a separate burette where saturation with water alone is possible.[2]

A simple experiment illustrates the combined effect of the error of solubility of the gaseous residue in the confining liquid and the change of the saturation pressure of this liquid. Large residues were collected and measured, and thereafter portions (1 to 5 ml) of fresh potassium hydroxide solution were admitted through the top cock of the burette. The diminishing volumes of the residues are given below:

Residue before admitting fresh KOH solution	Residue after admitting fresh KOH solution
ml	*ml*
86. 94	86. 40
86. 20	86. 04
86. 26	86. 10
86. 40	86. 14
86. 94	86. 80

[1] Martin Shepherd, BS J. Research **12,** 551 (1934) RP680.
[2] Martin Shepherd and E. O. Sperling, J. Research NBS **26,** 341 (1941) RP1380.

The rate of obtaining essential equilibriu between hydrocarbon residue and the "potassiu hydroxide solution" will depend upon the compos tion of the residue, degree and length of conta between residue and solution, temperature an composition of the solution, pressure of the res due, and such matters. A small amount residue leaves a long column of solution relativel isolated in the burette; a large volume may nearl empty the burette and discharge the solution the absorber where the mechanics of flow wi speed the approach to equilibrium.

The effect of these partial equilibria may appea during the initial analyses with fresh malei anhydride and fresh potassium hydroxide. Her is a series of analyses made under such condition (Sample 43–3):

Conjugated dienes
Percent
15. 32
14. 60
14. 43
14. 46
14. 17
13. 95
13. 98

The first residues were too small, because of th absorption of butenes and other hydrocarbons The indicated purities were correspondingly high at first.

With the same maleic reagent, but fresh KOH solution, these results were next obtained:

Conjugated dienes
Percent
14. 81
14. 68
14. 54
14. 55
14. 53
14. 50

Such behavior as this naturally causes errors when samples of differing composition are successively analyzed. The following examples illustrate what may be expected. The samples

examined contained approximately 95, 86, and 15 percent conjugated dienes, and they were analyzed in succession as reported below:

Fresh maleic anhydride and potassium hydroxide solutions were put into the apparatus and the "blank with CO_2" was obtained as follows:

Time elapsed	Residue
Minutes	*ml*
0	0. 22
10	0. 60
40	1. 06
70	1. 21
90	1. 42
110	1. 52
130	1. 60
150	1. 64
170	1. 68
190	1. 71
210	1. 74
250	1. 79
270	1. 81
290	1. 83
310	1. 85
340	1. 87
370	1. 88

Four analyses of sample P–6 were made. These results were obtained:

Conjugated dienes
Percent
[1] 86. 70
86. 31
86. 31
86. 29
86. 29

[1] Probably a mistake.

Next, four analyses of Sample DDC–8R–379 were made, and the results were:

Conjugated dienes
Percent
96. 10
96. 14
96. 18
96. 18

This was followed by four analyses of Sample P–6:

Conjugated dienes
Percent
86. 18
86. 11
86. 07
86. 09

Next, six analyses of Sample 43–3 were performed:

Conjugated dienes
Percent
15. 74
15. 38
15. 68
15. 33
15. 49
15. 11

With another change of maleic anhydride and potassium hydroxide, the following analyses were made in the order given:

	Conjugated dienes
	Percent
Sample P–6	86. 33
	86. 28
	86. 10
	86. 08
	86. 09
	86. 07
	86. 07
	86. 06
	86. 06
	86. 07
Sample 43–3	15. 64
	15. 22
	14. 69
	14. 76
	14. 40
	14. 37
Sample P–6	85. 47
	85. 77
	85. 93
	86. 06
	86. 11

From the above analyses it will be noted that:

1. A change in composition of the sample makes it necessary to set up a new equilibrium in the reagents before reproducibility is attained.

2. If this change in composition is not great, two or three analyses may establish the required new equilibrium.

3. If the change in composition is considerable, five or more analyses may be required to set up the requisite new equilibrium.

4. In going from a sample of relative high purity to one of lower purity, the initial analyses of the second sample will indicate too high a purity. The reverse effect is obtained by proceeding in the opposite direction. This is a natural consequence of the changes in physical equilibria previously discussed.

5. Freedom from the error caused by a changing vapor pressure of water with a change of composition of the system $KOH+K_2CO_3+H_2O$ is established in this experiment by the reproducibility attained at the end of each series of analyses, and the further fact that the final analyses of the second series of P–6 yielded the same values as the final analyses of the the first series of analyses of this sample, whereas the apparent amount of conjugated diene would have progressively decreased in the second series had the vapor pressure of the absorbing solution been progressively rising by a significant amount. The change in vapor pressure, however, would in time have introduced a large error. The solution should never be used until expended, but rather discarded at about half its useful life.

V. Physico-Chemical Equilibria in the Koppers-Hinckley Apparatus

The net chemical and physical behavior of the absorption processes in the Hinckley apparatus may be conveniently studied through analyses of both the original sample and the residue after absorption. Such analyses may be made with the mass spectrometer. Since the volume of both sample and residue for the Hinckley analyses are known, the volume of each component present in both sample and residue may be computed from their analyses. These data indicate how much of each component was correctly or incorrectly retained in the maleic absorber and confining fluid and how much of each was correctly or incorrectly delivered to the residue. A balance sheet composed from these data discloses at a glance how matters stand and offers a basis for correcting the volumetric analysis on the assumption that the analyses of both residue and original sample by the mass spectrometer are correct.

In some of the cases examined, these two analyses appeared to be consistent in most respects, and the volumetric determination of conjugated dienes can be brought into satisfactory agreement with the original analysis of the sample by the mass spectrometer if corrected in the manner indicated by the balance sheet. In some cases, however, more of one component may appear in the residue than existed in the original sample. This embarrassing excess must have been generated or contributed by either the mass spectrometer or the Koppers-Hinckley apparatus (or both) and because the source of this excess is not positively known its presence must for the moment be termed a minor miracle. However, it is possible to explain the excessive amounts of these components if we assume that: 1. No chemical or physical process within the Hinckley apparatus yielded the excess product, and, 2. the mass spectrometer is capable of yielding a better analysis of the impurities in a sample of 1,3-butadiene if the impurities are concentrated in a residue and this residue is analyzed. Thus the interference offered by large amounts of 1,3-butadiene is eliminated.

The latter assumption is certainly straightforward. The soundness of the first assumption depends primarily on the physical behavior of the Hinckley absorbers. There are times when it is apparent that equilibrium has not been attained; but it is equally true that definite enough equilibrium can be established and maintained, and a long series of results obtained with separate portions of a single sample of uniform composition will assure this fact. At such times, the too abundant appearance of a component in the residue may indicate the need to correct the composition of the original sample as measured by the mass spectrometer, by means of the mass spectrometer's analysis of the residue. This assumes that the maleic reagent has itself made no contribution to the residue through chemical reaction; and this assumption appears reasonable to organic chemists.

1. Equilibrium in the Analyses of Specification-grade Butadiene

The use of specification-grade samples permits comparison with the results obtained by the freezing point method, and this furnishes more data for the estimation of the accuracy of the Koppers-Hinckley method as relates to this particular grade of sample. For this reason, and because the apparatus was specifically designed for the analysis of this particular grade of butadiene, these analyses have been selected to study the physico-chemical equilibrium by the use of the spectrometer.

In the case of the samples examined, the compounds present in excess were primarily butenes. It does not appear likely that these were manufactured in the Hinckley apparatus, and the physical equilibria were so well adjusted that no sudden surge of butanes can be suspected. The residues were taken for analysis by the mass spectrometer after a blank had been obtained and after five to eight analyses agreeing to ± 0.01 percent had been made to establish satisfactory equilibrium in the Hinckley apparatus. Under these circumstances, the analyses of the residue by mass spectrometer would reasonably seem nearer to the true composition with respect to butenes than was the analysis of the original sample by mass spectrometer. If this is true, the mass spectrometer can be corrected by the mass spectrometer.

The data are tabulated in table 1. Column 2 gives the analysis of the residue by mass spectrometer, and column 3 gives the corresponding volumes of each component computed from the known volume of the residue and its composition. Column 4 gives the amounts of each component in the original sample of 100 ml. (The values are the same as the mole percents reported by the mass spectrometer). Columns 5 and 6 give, respectively, the amounts of each component correctly and incorrectly retained by the maleic reagent. Amounts appearing in column 6, therefore, represent plus corrections to be made to the measured residue. Columns 7 and 8 give the amounts of each component that were present in the residue, again correctly and incorrectly; column 8, therefore, represents a list of minus corrections to be applied to the measured residue. Column 9 notes the amounts of any components found in the residue that were not in the original sample.

TABLE 1. *Balance sheet showing amounts of each component before and after passing through the maleic absorber, according to the mass spectrometer*

Component	Residue from maleic absorber	Volume of original sample	Volume retained in maleic anhydride		Volume discharged to residue		Not in original sample [c]
			Correctly	Incorrectly [a]	Correctly	Incorrectly [b]	
	CYLINDER 55-15						
	Percent	*ml*	*ml*	*ml*	*ml*	*ml*	*ml*
1, 3-Butadiene	0.1	.....	97.82	97.82	.....	.....	.....
1, 2-Butadiene	.1	.....	.....	.....	.....	.....	.....
Propylene	1.9	0.04	0.05	.....	0.01	0.04	.....
1-Butene	30.2	.70	1.48	.....	.78	.70	.....
2-Butene	67.5	1.56	.58	.....	.....	.58	0.98
Total butenes	97.7	2.26	2.06	.....	.....	2.06	.20
n-Butane	0.4	0.01	0.03	.....	0.02	0.01	.....
Pentenes	.04	.....	.....	.....	.....	.....	.....
Pentadiene	.....	.....	.....	.....	.....	.....	.....
Dimer	0.02	.....	0.04	.....	0.04	.....	.....
Measured total	.....	2.31	.....	.....	.....	.....	.....
Total corrections	.....	.....	.....	.....	+0.07	.....	0.20
	CYLINDER 5-14						
1, 3-Butadiene	0.1	.....	98.14	98.14	.....	.....	.....
1, 2-Butadiene	1.5	0.03	.....	.....	.....	.....	0.03
Propylene	4.4	.09	0.06	.....	0.06	.....	.03
Total butenes	92.5	1.98	1.72	.....	1.72	.....	.26
n-Butane	1.5	0.03	0.04	.....	0.01	0.03	.....
Dimer	.....	.....	.05	.....	.05	.....	.....
Total	.....	2.14	.....	.....	+.06	.....	0.32
	CYLINDER 11-20						
1, 3-Butadiene	0.1	.....	98.62	98.62	.....	.....	.....
1, 2-Butadiene	.1	.....	.....	.....	.....	.....	.....
Propylene	.....	.....	0.03	.....	0.03	.....	.....
Total butenes	99.1	1.49	1.32	.....	.....	.....	0.17
n-Butane	0.2	.....	0.02	.....	0.02	.....	.....
Dimer	.9	0.01	.02	.....	.01	.....	.....
Total	.....	1.51	.....	.....	.06	.....	.....
	CYLINDER 86-2 RuR-SR						
1, 3-Butadiene	1.7	0.03	97.97	97.94	.....	0.03	.....
1, 2-Butadiene	2.0	.04	0.17	.....	0.13	0.04	.....
Propadiene	2.0	.04	.....	.....	.....	.....	0.04
Propylene	0.2	.....	0.03	.....	0.03	.....	.....
Total butenes	94.1	1.87	1.82	.....	1.82	.....	0.05
Pentenes	0.02	.....	.....	.....	.....	.....	.....
Dimer	.05	.....	0.05	.....	0.05	.....	.....
Total	.....	1.98	.....	.....	+0.21	−0.03	0.09

See footnotes at end of table.

TABLE 1. *Balance sheet showing amounts of each component before and after passing through the maleic absorber, according to the mass spectrometer*—Continued.

Component	Residue from maleic absorber	Volume of original sample	Volume retained in maleic anhydride		Volume discharged to residue		Not in original sample [c]
			Correctly	Incorrectly [a]	Correctly	Incorrectly [b]	
CYLINDER 55-17							
	Percent	*ml*	*ml*	*ml*	*ml*	*ml*	*ml*
1, 3-Butadiene	0	.....	98.30	98.30	.....	.....	.....
Butenes	99.2	1.46	1.61	.....	0.15	1.46	.....	.....
Propylene	0.1	0.015	0.03	.....	.015	0.015	.....	.....
Butanes	.2	.03	.02	.....	.....	.03	.....	0.01
Vinyl cyclohexene	.1	.015	.04	0.025	.....	.....	0.015	.....
Pentene	.1	.015	.....	.....	.....	.015	.....	0.015
Dimethyl ether	.2	.03	.....	.....	.....	.03	.....	.03
Ethyl alcohol	.1	.015	.....	.....	.....	.015	.....	.015
Total	100.0	1.47	(measured)					

[a] These values correspond to plus corrections (See text).

[b] These values correspond to minus corrections (See text).

[c] These components were not present in the original sample and therefore are of undetermined origin.

Note: If the dimer is not removed from original sample, the Hinckley analysis will be in error (unless corrected), but it cannot be said from the chemical viewpoint that the dimer is "incorrectly retained" by the maleic anhydride.

The balance sheet for each sample may be briefly considered.

In the case of sample 55–15, no significant amount of 1,3-butadiene was found in the residue. A trace of 1,2-butadiene not found in the original sample is reported in the residue—but the amount is not significant. Of the 0.05 ml of propylene found in the sample, 0.04 ml appeared correctly in the residue, leaving 0.01 ml incorrectly retained in the maleic reagent. (Actually, this is not a significant difference but is mentioned to illustrate the method of computing.) Of the 1.48 ml of 1-butene reported in the sample, only 0.70 ml was found in the residue, indicating 0.78 ml as incorrectly retained in the maleic reagent. On the other hand, of the 0.58 ml of 2-butene reported in the sample 1.56 ml bobs up in the residue, an excess of 0.98, which is listed in column 8. This picture with respect to the butenes appears out of line. It seems more plausible to consider the butenes as a group rather than individually, and this certainly gives a cleaner analysis. Computed on this basis, there remains 0.20 ml of total butenes in excess of the amount present in t sample. If 2.26 is accepted as a better value total butenes in the original sample than the 2 reported, the corrected value, 97.62, agr exactly with the value obtained by the freezi point. Continuing as before, only 0.01 ml of original 0.03 ml of *n*-butane appears in the re due, and no significant amount of the origi 0.04 ml of dimer appears in the residue. T latter is, of course, to be expected and should corrected. Ignoring the butenes as individua this leaves a balance of 0.07 ml plus correct and no minus correction. The residue measur was 2.31; the correct residue is 2.38; and the butadiene, correspondingly corrected, is 97. Thus the freezing point, mass spectrometer, a method L. M. 2.1.1.7 can be brought into extra dinary agreement.

In the case of sample 5–14, a total of 0.32 ml butenes, propylene, and 1,2-butadiene appears the residue in excess of the amounts reported f the sample. The original analysis by mass spe trometer gives a corrected value of 97.83 perce of 1,3-butadiene. The volumetric analysis correct for components incorrectly retained in the male anhydride yields the value 97.80. But the freezi point value is 97.98.

The balance sheet for sample 11–20 gives clos agreement. Corrected for the more modest exce of 0.17 ml of total butenes, the original ma spectrometer value becomes 98.45. The vol metric value, corrected for 0.06 ml incorrect retained in the maleic reagent, becomes 98.43. Th freezing point gave 98.48.

The results from sample 86–2 are not so sati factory. Originally there was fine agreemen between the three methods; but a large correcti for components incorrectly retained in the male reagent lowers the volumetric value to 97.8 There is also a minor excess of 0.09 ml, whic lowers the mass spectrometer value to 97.88. Th freezing point remains frozen at 97.99.

In the case of sample 55–17, the balance she shows no significant amount of any compound i the residue not originally present in the sample Some of the butene fraction originally present di not appear in the residue, and the Hinckley resul can thus be corrected from 98.53 to 98.38 percent The analysis of the original sample by the mas spectrometer was 98.30. There was no measure ment of the freezing point.

The original and corrected data are tabulated in table 2. Columns 2, 3, and 4 give the original values obtained by the freezing point, mass spectrometer, and volumetric (L. M. 2.1.1.7) methods, respectively. Column 5 gives the volumetric value corrected by the mass spectrometer in the manner just described. Column 6 gives the mass spectrometer value corrected by the combined Hinckley-mass spectrometer procedure, also just described.

TABLE 2. *Analyses of specification grade 1,3-butadiene by freezing point, mass spectrometer, and Hinckley method*

Sample	Freezing point	Mass spectrometer	L. M. 2.1.1.7	L. M. 2.1.1.7 corrected by Mass spectrometer	Mass spectrometer corrected by Hinckley-mass spectrometer
	Percent	*Percent*	*Percent*	*Percent*	*Percent*
[illegible]5	97.62	97.82	97.69	97.62	97.62
[illegible]4	97.98	98.14	97.87	97.80	97.83
[illegible]0	98.48	98.62	98.50	98.43	98.45
[illegible]2	97.99	97.97	98.02	97.84	97.88
[illegible]7	None	98.30	98.53	98.38	.....

If we arbitrarily consider differences of less than 0.1 percent as agreements, we find the following such agreements in the first four samples reported:

Original freezing point with original mass spectrometer	1
Original freezing point with original L. M. 2.1.1.7	3
Original mass spectrometer with original L. M. 2.1.1.7	1
Original freezing point with corrected mass spectrometer	2
Original freezing point with corrected volumetric	2
Original mass spectrometer with corrected volumetric	0
Corrected mass spectrometer with corrected volumetric	4

These comparisons do not seem to provide sufficient reason for purchasing a Koppers-Hinckley apparatus to correct a mass spectrometer, or a mass spectrometer to correct a Koppers-Hinckley apparatus, or either to correct a freezing point. They do suggest a more realistic attitude with regard to analytical tolerances.

2. Effect of the Amount of Diamylamine Inhibitor in the Maleic Anhydride

Amounts of diamylamine varying from 1 to 7 percent have been recommended. The three concentrations favored by various laboratories were tested: 1 percent, 2 percent and 7 percent. The original ampoules of maleic anhydride supplied with the apparatus (supposedly official) contained 50 g of the reagent. This amount was first used, but afterward it was increased to 65 g (Hinckley's recommendation). A sample containing approximately 96 percent of 1,3-butadiene was used throughout these measurements. It was selected because it contained 1,2-butadiene and apparently the majority of the "difficult" components (styrene excepted). The sample and residues were analyzed by the mass spectrometer, and these analytical data, together with the analyses by the Hinckley method, are shown in table 3. This table is arranged in the same manner as the previous tabulated balances, except that the volumes (in ml) of each component found in the residue appear in a single column. The algebraic signs indicate corrections.

The data show notable amounts of 1,3-butadiene escaping the maleic reagent that contains only 1 percent of diamylamine; and this error was larger with 50 g of reagent than with 65 g of reagent. Results with the reagent containing 7 percent of diamylamine are too confused to mean anything. There were large amounts of almost all of the components present in the residue that were not found in the original sample. Check observations yielded the same story, and an analysis of the "blank", or gases collected after this series of analyses and during the subsequent continued passage of carbon dioxide through the reagent, again showed the presence of components not originally in the sample. A long series of analyses yielded no satisfactory reproducibility, and the 7-percent variant was accordingly discarded along with the 1 percent. The reagent with 2 percent of diamylamine did not give a perfect performance, but there were no greatly embarrassing excesses, and the results could be coordinated with those of the mass spectrometer. The Hinckley analysis, corrected by means of the mass spectrometer, gave the result: 95.62 percent conjugated dienes—a very satisfactory agreement.

Just how the "inhibitor" functions is not entirely

known. The analyses indicate that less 1,2-butydiene is retained by the reagent containing 2 percent of the inhibitor than is retained by the 1-percent variant; but the 7-percent variant yielded no 1,2-butadiene to the residue. Instead, an embarrassing increase in both butanes and butenes is noted. Whatever the chemical picture, it seems that the change in surface tension of the maleic solution with addition of the diamylamine inhibitor results in the formation of smaller bubbles of ascending gas and that the 2-percent variant is more suitable in this respect than the 1 percent. Herein may lie its real contribution.

Other analyses reported herein, including those of section V, 1, were done with 65 g of the maleic anhydride containing 2 percent of diamylamine.

TABLE 3. *Effect of the diamylamine inhibitor*

Component	Composition of original sample by mass spectrometer	Results with 1 percent inhibitor 50 g of reagent			Results with 1 percent inhibitor 65 g of reagent			Results with 2 percent inhibitor 65 g of reagent		Results with 7 percent inhibitor g of reagent	
		Hinckley analysis of original sample	Analysis of residue by mass spectrometer	Amount of component in residue	Hinckley analysis of original sample	Analysis of residue by mass spectrometer	Amount of component in residue	Analysis of residue by mass spectrometer	Amount of component in residue	Analysis of residue by mass spectrometer	Amount of component in residue
	Percent	*Percent*	*Percent*	*ml*	*Percent*	*Percent*	*ml*	*Percent*	*ml*	*Percent*	*ml*
1,3-Butadiene	95.60	96.40	10.0	[a]−0.36	96.35	4.6	[a]−0.17	0.1		0.2	−0
1,2-Butadiene	1.11		9.0	[b]+.32		14.3	[b]+.52	16.1	[b]+0.59		
Propadiene	0.18		8.6	[c].31		3.1	[a]−.11	3.7	[a]−.14	0.5	−0
Propylene	.08		1.7	+.06		1.8	[b]+.07	1.8	[b]+.07	1.6	
Propane											
1-Butene	2.24		53.0	[b]+1.91		63.5	[c]2.32	57.9	[b]+2.14	35.5	[c]1
2-Butene	0.68		17.0	[b]+0.61		12.0	+.44	18.5	0.69	32.1	[c]1
n-Butane	.08		0.5	[b]+.02		0.5	+.02	0.5	[b]+.02	24.0	[c]2
i-Butane										4.9	[c]0
Pentadiene			0.01			0.02		0.02			
Pentenes			.1			.1		1.1	[b]+0.04	4.9	[c]0
Pentanes										0.6	[c]
Vinylcyclohexene						.1		0.4	.01	.1	

[a] Should not have been in the residue.

[b] All of the component should have been delivered to the residue, but the amount represented by the difference between the total originally present and that found in the residue was incorrectly retained in the absorption system.

[c] More of the component was found in the residue than was found in the original sample. (The excess is the difference between the two.)

3. Effect of Rate of Flow of the Sample Through the Maleic Absorber

The rate of flow specified is 35 cc of carbon dioxide sweeping gas per minute. Four rates were tried: 10, 35, 80, and 100 cc/minute. Analyses of the residue by the mass spectrometer are tabulated below:

TABLE 4. *Effect of rate of flow of sweeping gas*

Component	Original sample	Residue			
		Flow, 10 cc/min	Flow, 35 cc/min	Flow, 80 cc/min	Flow, 100 cc/min
	Percent	*Percent*	*Percent*	*Percent*	*Percent*
1,3-Butadiene	95.60	0.1	0.1	0.1	0.1
1,2-Butadiene	1.11	16.2	13.9	15.6	16.2
Propadiene	0.18	3.7	6.7	6.0	6.6
Propylene	.08	1.8	2.1	1.5	1.2
1-Butene	2.24	58.4	60.4	59.6	58.3
2-Butene	0.68	18.7	16.0	16.4	16.9
n-Butane	.08	0.5	0.6	0.6	0.5
Pentenes		.1	.2	.1	.2
Pentadiene		.02		.1	
Vinylcyclohexene		.4	0.2	.1	0.1

From these data it may be concluded that 35 cc per minute is a very safe rate for the sweeping gas. Indeed, were it not for the fact that fritted disks such as are used to break up the gas stream entering the absorber vary somewhat in their performance, it would be well to increase the recommended rate and so shorten the time required for a determination. (An analysis at the 10 cc/min rate required over an hour; that at the recommended 30 cc/min required 22 minutes; but the one made at 80 cc/min took only 10 minutes.) However, the safe rate should be determined for each fritted disk used if any departure from the instructions is contemplated.

VI. Accuracy and Reproducibility

The accuracy obtained in analyzing specification-grade butadiene can be estimated by comparison with the results obtained by the mass spectrometer and the freezing-point method. These have been previously noted (table 1) and

indicate that a value ±0.2 percent of the whole may be expected. No good estimation of accuracy can be made for samples of lesser purity.

When the apparatus is operating correctly, the reproducibility to be expected with each type of sample may be given as follows:

Conjugated dienes	Approximate reproducibility (percent by volume of the whole)
Percent	
98.5 or better	±0.01
85 to 95	±0.02 to ±0.2 [1]
2 to 15	±0.4

[1] Depending upon the composition with respect to C_5 and C_4 hydrocarbons that may interfere with the reaction.

Typical anslyses illustrating the attainable reproducibility have already been given in previous sections of this report. Others follow to supplement the range of composition not previously covered.

TABLE 5. *Analyses illustrating attainable reproducibility*

Condition	Lot [a]	Conjugated dienes	Analyst
	SAMPLE 55-15		
		Percent by volume	
Not dried	B	97.67	MS.
	B	97.68	MS.
	B	97.68	MS.
Dried over indicating drierite	A	97.68	RLT.
	C	97.67	RLT.
	C	97.68	RLT.
	C	97.68	RLT.
	C	97.70	RLT.
	D	97.70	MS.
	D	97.70	MS.
	D	97.70	MS.
	D	97.70	MS.
Average		97.69	
Average deviation from average		±0.01	
	SAMPLE 5-14		
Not dried	A	97.89	RLT.
	A	97.90	RLT.
	A	97.89	RLT.
	A	97.88	RLT.
Dried over indicating drierite	B	97.85	RLT.
	B	97.86	MS.
	B	97.86	MS.
	B	97.87	MS.
	C	97.87	MS.
	C	97.87	RLT.
	C	97.87	RLT.
	C	97.87	RLT
Average		97.87	
Average deviation from average		±0.01	

See footnote at end of table.

TABLE 5. *Analyses illustrating attainable reproducibility*—Continued

Condition	Lot [a]	Conjugated dienes	Analyst
	SAMPLE 11-20		
		Percent by volume	
Not dried	A	98.49	SS.
	A	98.48	SS.
	A	98.48	SS.
	A	98.48	SS.
Dried over indicating drierite	B	98.51	MS.
	B	98.51	MS.
	B	98.51	MS.
	B	98.51	MS.
	C	98.50	MS.
	C	98.48	SS.
	C	98.49	SS.
Average		98.50	
Average deviation from average		±0.01	
	SAMPLE 86-2		
Not dried	A	97.99	SS.
	A	98.00	SS.
	B	98.01	SS.
	B	98.02	SS.
Dried over indicating drierite	C	98.03	RLT.
	C	98.05	RLT.
	C	98.05	RLT.
	D	98.03	RLT.
	D	98.01	RLT.
	D	98.00	RLT.
	D	98.02	RLT.
Average		98.02	
Average deviation from average		±0.01	
	SAMPLE 43-3		
Not dried	A	15.1	MS.
	A	14.9	MS.
	A	14.9	RLT.
	A	14.7	RLT.
Average		14.9	
Average deviation from average		±0.1	
Not dried	B	14.0	RLT.
	B	14.0	RLT.
	B	14.0	RLT.
	B	13.9	RLT.
Average		14.0	
Average deviation from average		±0.03	

See footnote at end of table.

TABLE 5. *Analyses illustrating attainable reproducibility*—Continued

Condition	Lot [a]	Conjugated dienes	Analyst
		Percent by volume	
SAMPLE 43-3			
Not dried	C	15.0	RLT.
	C	14.9	RLT.
	C	14.5	RLT.
	C	14.2	RLT.
Average		14.7	
Average deviation from average		±0.3	
Not dried	G	14.4	RLT.
	G	14.2	RLT.
	G	14.0	RLT.
	G	14.0	RLT.
Average		14.2	
Average deviation from average		±0.2	
Not dried		15.2	RLT.
		14.7	RLT.
		14.8	RLT.
		14.4	RLT.
		14.4	RLT.
		15.6	RLT.
		15.3	RLT.
Average		14.9	
Average deviation from average		±0.4	
SAMPLE PL-132-11			
Not dried	A	1.3	RLT.
	A	1.8	RLT.
	A	2.0	RLT.
	A	1.6	RLT
	A	1.4	RLT.
Average		1.6	
Average deviation from average		±0.3	

[a] When the sample number is followed by a letter, the sample was taken into the Hinckley sampler, and samples with the same letter are of the same composition. Thus, the lettered samples give a measure of the reproducibility of the analytical procedure. Samples identified by number only are drawn individually from the cylinder into the measuring pipette of the apparatus. Thus, any change in composition upon sampling which intrudes into the analytical picture may be estimated by comparing groups of different letters, or samples identified by number only, once the reproducibility of the analytical method is measured.

VII. Notes on the Operating Characteristics of the Koppers-Hinckley-Podbielniak Apparatus

1. Occasional Erratic Behavior

Even the best of all possible apparatus will sometimes indulge in the perversity practiced by inanimate objects, and the present apparatus is no exception. The following experiment, which started as a series of analyses, to illustrate the vagaries of sampling, disclosed more than was originally intended. The initial conditions were as listed below.

The apparatus was working correctly in all visible respects. The maleic reagent had been used for nine analyses, (five of a sample containing about 2 percent of conjugated dienes and four of a sample containing about 96 percent of conjugated dienes,) and had given reproducible results in both cases. A fresh solution of potassium hydroxide had been put into the absorber burette. A blank had been obtained. The analysis of sample BB–574, Phillips Hydro-carbon Mixture No. 6, was then undertaken. The cylinder was connected to the measuring pipette of the apparatus by means of a 120-degree stopcock and nitrometer tubing. This arrangement permitted flushing the sampling line with mercury from the pipette and with gas from the cylinder.

This is what happened:

1. With the cylinder vertical, valve at top, and sampling from the vapor phase, 6 analyses yielded the values

Conjugated dienes
Percent
82.56
82.17
82.68
83.25
83.29
83.12
Avg. 82.85±0.4

2. The position of the cylinder was then reversed, and with valve at bottom "sampling

from the liquid phase," 9 analyses yield the values

Conjugated dienes
Percent
82. 80
83. 60
83. 48
83. 52
81. 75
81. 44
82. 98
82. 73
80. 57
Avg . . 82. 54±0. 2

3. A sample was then drawn from the inverted cylinder into the Hinckley sampler, so that four analyses of the *same* mixture could be made. These analyses yield the values

Conjugated dienes
Percent
80. 76
82. 35
82. 33
84. 72
Avg . 82. 54±1. 09

These results are worth a moment's reflection. Series 1 was not expected to check series 2, although closer agreement was expected within each series. Series 3 was then made to show whether the divergence of individual results was caused by sampling or by the performance of the analytical apparatus. Apparently the divergence could not be blamed upon sampling, for series 3 indicated that the apparatus was not yielding reproducible results. The cause was not apparent. Operation was normal in all respects except that the normal operating back pressure had increased from 7 to 9 psi, which is well within the limit set by the mercury relief seal. The joints were examined and appeared to be well lubricated. They were wiggled about with no apparent change. The joints were then tested for leaks by soap solution, and no leaks were detected. These tests were repeated several times, and nothing was found out of order.

The solution of potassium hydroxide was replaced, and during the run for a blank the back pressure suddenly rose to the point of blowing the relief seal. The joints were disconnected and all lines found free, but the maleic-filled absorber was plugged. The maleic reagent could not be withdrawn from the bottom of the absorber even when vacuum was applied. It was withdrawn from the top, and a solid plug below the sintered plate was removed by dissolving in acetone. The absorber was cleaned with acetone, dried by a current of air, and a fresh charge of the maleic reagent put into it. The lines were again connected, a blank was obtained, and analyses of the same sample resumed. This time the following results were obtained:

4. With the inverted cylinder (valve at bottom) three separate lots were taken into the Hinckley sampler. These analyses yielded the values

	Conjugated dienes
	Percent
Lot A	85. 93
	85. 95
	85. 97
	85. 94
	Avg . 85. 95±0. 01
Lot B	86. 08
	86. 09
	86. 09
	86. 08
	Avg . 86. 09±0. 01
Lot C	86. 12
	86. 10
	86. 10
	Avg . 86. 11±0. 01

5. With the cylinder inverted and connected as before to the measuring pipette, so that each sample was individually drawn from the cylinder, these values were obtained:

Conjugated dienes
Percent
86. 08
86. 28
86. 38
86. 98
86. 07
Avg . . . 86. 16±0. 14

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6. The balance of the sample from lot C was then analyzed. (The Hinckley sampler had been filled under slight pressure in order to yield a sufficient amount for six analyses). The values obtained were:

Conjugated dienes
Percent
86. 10
86. 14
86. 09
Avg---86. 11±0. 02

7. The inverted cylinder was again connected to the apparatus directly, and a series of individual samples were withdrawn and analyzed. The values yielded were:

Conjugated dienes
Percent
86. 13
86. 15
86. 33
86. 28
86. 10
86. 08
86. 09
86. 07
86. 07
86. 06
86. 07
Avg---86. 13±0. 07

The results of series 4 to 7, inclusive, may now be compared. Series 4 shows the apparatus giving a pleasing reproducibility. The individual results of each lot, A, B, and C, are in excellent agreement with themselves. Lot A differs from the other two by 0.15 percent, and this difference may be tentatively assigned to the vagary of the sampling procedure. The following series 5 was intended to estimate the extent of chance change of composition during sampling. Differences were found, the largest variation being 0.4 percent. Series 6 was designed to tie back to series 4, to show that the analytical apparatus was still performing in a trustworthy manner. Since series 6, lot C, came from the same sampler as series 4, lot C, the apparatus was yielding consistent results. Therefore, the divergence observed in series 5 may be tentatively assigned to the vagary of the sampling procedure. Series 7 was designed to explore this vagary further. The procedure used were the same as employed for series 4. The analyses in this series show both divergence and close agreement depending on the part of the list selected.

Although the data obtained indicate that sampling is erratic (a subject to be mentioned briefly at the end of this report), the immediate problem is with respect to the erratic behavior of the Koppers-Hinckley-Podbielniak apparatus itself. Except for a difference of 2 psi in operating pressure, which was not at first considered significant, there was no outward or visible difference in operation of the analytical apparatus throughout the entire series, 1 to 7 inclusive. There was no reason for the analyst to believe that the apparatus was not giving good results at first, except that the results themselves were not as consistent as he supposed they should be. Until series 3, there was no positive evidence that the apparatus was giving poor analyses. Except for the change in back pressure, the actual operating characteristics, in so far as one could perceive, were the same for both series 3 and 4. Series 5 complicates the problem by introducing a different order of reproducibility than that obtained by each individual lot of series 4. Faced with such data, the analyst does not know how to measure the performance of the apparatus even in terms of reproducibility of the results obtained, *unless he always uses the Hinckley sampler and performs many analyses for each sample examined.* His problem, then, becomes essentially one of finding the time to do a decent analysis of all samples submitted to him.

The importance of employing a sample container capable of delivering at least five successive portions of the same composition for analysis cannot be too greatly stressed. The foregoing experiment shows that the performance of the apparatus with respect to reproducibility cannot be measured otherwise, and that this performance must be measured if the operator is to have any assurance of just where he is.

Further experience with the apparatus indicated that an increasing back-pressure was often accompanied by poor reproducibility. If the restriction occurred in the maleic-filled absorber, this was always the case. Evidently the reagent is spoiled

y excessive water vapor or some of the heavier ydrocarbons. This may happen frequently, and hen it does the warning of the pressure gage is sually the only indication of trouble, for the ppearance of the reagent is not enough for a iagnosis. In itself, this warning is inadequate. ence, an actual measure of reproducibility must e retained. Unfortunately there seems to be no ndency on the part of RuR users to hold to is essential.

2. Introduction of the Sample into the Apparatus

Since there are two methods for introducing the ample they should be considered separately.

(1) The first method (which we greatly prefer) nvolves the use of the special sampling tube upplied with the apparatus. This tube is connected to the mercury sump of the apparatus by means of an interchangeable grinding. Interposed between the female grinding sealed to the sump and the male grinding sealed to the sample tube is a male-female grinding drilled with appropriate holes. The intermediate grinding may be rotated with respect to either of the other two, and the grinding on the sampling tube may be rotated with respect to the intermediate grinding. All of the necessary connections can thus be achieved.

This system is not conventional and is therefore mildly confusing at first glance. The written explanation of its operation, while perfectly clear, is apt to leave one's eyes and hands in some doubt during the initial experience. Actually, the system is perfectly simple, and its operation is easy enough. It could be taught, by demonstration, to nontechnical personnel.

After going through the necessary motions two or three times, the operation of this sampler is not only simple, but it offers a convenient service. Where there is any doubt about change of composition on sampling from a cylinder under pressure—and this doubt must always exist for many types of samples until it can be demonstrated that separation does not occur with each type of sample—the sampler can be used to establish *reproducibility* to the extent of four to six samples of the same composition. Thus it may be possible to withdraw one lot of say four samples from a cylinder, make four determinations in good agreement, and then withdraw a second lot of four samples whose analyses are again in agreement with themselves but not necessarily in agreement with the first lot.

The Hinckley sampler may be used in three ways:

1. If it can be flushed with sample and thereafter connected to the apparatus, the procedure is simple enough. However, specific directions should be given to insure complete flushing and such directions would involve a measurement of displacing gas in terms of volume or of time at a measured rate of flow. The latter combination is preferable since it fixes at least vaguely the reproducibility of the sampling.

2. It can be filled with mercury which the sample will later displace. (In this event, a 120-degree cock should be connected to the inlet to permit flushing of the sampling line with mercury from the sampler and with gas from the cylinder or source of sample, and a tee should be connected to a mercury seal of somewhat over barometric height.)

3. It can be evacuated prior to filling with sample. In case this is done, the sample should be supplied at such a rate that no excessively reduced pressure occurs in the sampling line.

The second method of sampling is to connect the source directly to the apparatus with the sampler displaced by a stopcock key. Again the 120-degree cock appended to the system will permit flushing the sampling line first with mercury from the apparatus and then with sample from its source. This cock amounts to a necessity in so far as we are concerned. The operations are simple. The procedure of sampling directly into the apparatus is poor, since a separation of the sample en route to the apparatus may alter its composition.

3. Venting

When the sample for analysis has been transferred from the Hinckley sampler under some pressure to the measuring pipette, a necessary step in the actual measurement of this sample is to turn the sampler to connect the pipette to the mercury sump, which is vented to the atmosphere through a small hole at the front of the sump. If the three bores involved become plugged with lubricant when the grindings are turned to make the necessary connections, the amount of sample is not known. A slightly generous use of the very viscous lubricant sup-

plied with this apparatus, combined with the pressure exerted downward by the weight of mercury within the sampler (which tends to cause the lubricant to exude), has actually produced plugs of lubricant that interfere with measurement of the sample. When this happens, there is no decisive way of knowing it. Usually when the sample is properly vented, there are one or more indications that venting has actually occurred: a bead of mercury may be blown from the bores; the rush of excess sample into the sump is audible; the presence of excess sample in the atmosphere can be detected by its distressing odor. Sometimes no one of these three portents are perceived. A side tube projecting from the vent hole, to which is affixed a short length of smallish diameter rubber tubing terminating in a short length of glass tube which dips just under the surface of the water in the jacket surrounding the measuring pipette, is very helpful. Then, if excess pressure is relieved, it is positively indicated by escaping bubbles. If no bubbles appear, the operator knows that the connection is plugged; or if water is drawn into the tube, the operator knows that excess pressure was never achieved upon drawing the sample into the measuring pipette. (This has happened when the mercury levels in the leveling bulbs belie the fact.)

Errors caused by failure to vent are interesting, because they can travel to the right or left of center (speaking graphically). Thus, if excess pressure is not vented to atmosphere the sample will be too large by an indeterminate amount, the consequent residue too large, and the corresponding purity too low. But if excess pressure has not been achieved in sampling, one of four conditions may be obtained.

1. If the bores are plugged, the sample is too small by an indeterminate amount and the purity is correspondingly too high.

2. If the bore is not plugged and the sump happens to be filled with air when the pipette is connected thereto, the residue will be too large by the amount of air drawn into the pipette, and the purity correspondingly too low.

3. If the bore is not plugged and the sump is filled essentially with carbon dioxide, which represents the usual operating condition *after* the *first* analysis for the day, the sample will be diluted with carbon dioxide and will be correspondingly too small, with a purity correspondingly too high.

4. Finally, if the sump is filled with carbon dioxide that contains any appreciable amount of the previous sample, the purity obtained may be either high or low, depending upon the proportion of sample in the sump and its composition with respect to the composition of the sample to be analyzed.

The connection to the water bath could eliminate these uncertainties.

4. Detection of Leaks

The instruction manual supplied with this apparatus states: "Leaks will be troublesome unless great care is taken to have a tight system. Careful greasing of stopcocks and joints and tight connections are necessary." This is quite true.

There are two procedures ordinarily used to detect and guard against leaks. The first, and perhaps the most generally used, procedure is based upon the optimistic assumption that there are no leaks. When this procedure is used, leaks are detected by inductive reasoning. Thus the analyst may proceed from result to result until it becomes apparent that results do not check and he suspects, finally, that something has happened to the apparatus. For the present this procedure is presumably to be used with method L. M. 2.1.1.7. To a certain extent, this is inescapable for leaks may occur at any time during the course of any analysis. At any rate, once the leak is suspected it should be detected and repaired and not simply repaired by completely reassembling the apparatus in the hope that this time it went together tightly.

The second procedure is to test for leakage prior to use, during use, and after use, if anything important is involved. This assumes that if the analysis is done at all there was some good reason for it. This procedure has so much to recommend it to those who want correct answers that it in turn is strongly recommended for inclusion in L. M. 2.1.1.7. The question, then, is what test or tests can be employed?

If the apparatus is assembled without reagents, pressure can be applied to unbalance the mercury seal between the KOH-filled absorber and the outlet of the maleic-filled absorber. A return of the mercury up the capillary tube then indicates leakage. But to apply this test, the apparatus must be dry and free of reagent. The test is according-

y costly in time and effort and is hardly the thing o use during a series of analyses.

With the maleic reagent in the absorber no eak test based upon a change in pressure seems ossible, since notable interference may be ex- ected from absorption or desorption. A bypass cross the maleic absorber would permit testing of he glass-to-metal spherical joints, which are the ost apt to give trouble. Certainly a suitable eak test should be devised for use during actual peration, or for use between analyses with all eagents in place. And this test should be made ith the apparatus under operating pressure, not nder reduced pressure.

5. Mercury Hazard

The Koppers-Hinckley-Podbielniak apparatus presents a potential mercury hazard. The air about the apparatus was examined with Woodson's optical mercury vapor detector (a General Electric instrument). Normal operation will usually deposit enough mercury on the various heated surfaces of the Koppers-Hinckley-Podbielniak unit to furnish concentrations of mercury vapor in air around the apparatus greater than 250 $\mu g/m^3$. The allowable limit, according to the National Institute of Health, is 100 $\mu g/m^3$. Notable amounts of mercury have been found excreted in the urine of several workers exposed to 20 $\mu g/m^3$. When the heated surface of the Koppers-Hinckley-Podbielniak apparatus were cleaned and mercury kept from them, the concentration eventually dropped to about 50 $\mu g/m^3$. However, the cleaned surfaces do not represent average laboratory conditions. The apparatus cannot be operated without occasionally depositing some mercury on the hot spots.

VIII. Notes on Sampling

It has long been known that special procedures are required to capture a true sample of the confined liquid phase of a two (or more) component system boiling below atmospheric temperature at existing atmospheric pressure (and not azeotropic). The procedures may be outlined:

1. The liquid phase is made homogeneous.
2. A sufficient portion of the liquid phase is isolated from the bulk of the mixture, without a change of composition of the mixture and hence without boiling.
3. This isolated portion of the liquid phase is completely evaporated into a suitable container, again without change of composition.
4. The resulting vapor is made homogeneous.

It is of course perfectly obvious that the composition of the vapor above the liquid does not represent the composition of the liquid, and that it is constantly changing over the course of the evaporation of the liquid. It has also been found that significant changes of composition occur when the liquid itself is removed through a tube that remains open to the bulk of the liquid during the process of sampling. Thus the composition of a sample of liquid removed by withdrawing into a capillary tube depends upon the rate of sampling, the bore of the tube, and even the material of the tube, as well as the ordinary conditions of temperature, pressure, and composition of the liquid.

If sampling occurs from a closed system in which the liquid is under pressure, notable separation is sometimes achieved. Such separation is astonishingly large for systems such as nitrogen-methane, which occurs in helium stills, and the behavior of this mixture has served to magnify the effect to be expected in the butadiene mixtures. Withdrawal "from the liquid phase" of an inverted cylinder is always accomplished at the cost of some degree of separation at the valve. Whether or not this is significant must be determined before any reliance can be placed in any analytical data from any source. From such observations as have been made in connection with this study, it would seem reasonable not to worry too much about separation of the specification grades. Undoubtedly it occurs, but as a matter of arithmetic it does not matter. However, the worry is apparent when the "purity" of the sample has been dropped to 85 percent, as was the case with sample P-6.

Until the sample containers themselves are equipped with a suitable device for isolating a true sample of the liquid, much time will be lost in a fruitless comparison of analytical results from various laboratories.

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Measurements of Heat of Vaporization and Heat Capacity of a Number of Hydrocarbons

By Nathan S. Osborne* and Defoe C. Ginnings

Using a new calorimeter, accurate measurements have been made of the heat capacities of twelve hydrocarbons in the range 5° to 45° C, and of the heats of vaporization of fifty-nine hydrocarbons at 25° C. These hydrocarbons, having from 5 to 10 carbon atoms per molecule, include 35 paraffins, 3 alkylcyclopentanes, 10 alkylcyclohexanes, and 11 alkylbenzenes.

I. A Calorimeter for Measuring Heat of Vaporization and Heat Capacity

1. Introduction

The design of a calorimeter is a very important factor in obtaining reliable results. In designing the present calorimeter, there were three principal considerations. First, the calorimeter shell should be made small because some of the hydrocarbons were available in relatively small amounts. Second, the measurements (especially vaporization) should be accurate to at least 0.1 percent. Third, the apparatus should permit relatively rapid measurements so that a large number of materials could be investigated. Making the calorimeter small has certain other advantages besides allowing the use of small samples of hydrocarbons. In a small calorimeter, it is possible to dispense with mechanical stirring and to distribute heat by a system of copper vanes. These vanes minimized the time required for thermal equilibrium and contributed both to accuracy and ease of operation. Another advantage of a small calorimeter is that it is possible to use metal shields to obtain isothermal surfaces for the control and evaluation of heat leak. This contributes to the accuracy of the results as heat leak is usually an important source of error.

2. General Description of Method and Apparatus

The principles of the method that was used with this apparatus have been described in previous publications [1].[1] The method was applied previously [2, 3, 4] to measurements on saturated water and steam from 0° to 374° C.

The apparatus consists essentially of a calorimeter in which a sample of the fluid may be so isolated that its amount, state, and energy may be accounted for. The sample or a definite part thereof may be made to pass through a rise of temperature or may be evaporated and withdrawn at a constant temperature while the accompanying gain or loss of energy is determined.

The sample, part liquid and part vapor, is enclosed in a metal calorimeter shell. An electric heater on this shell provides a means of adding measured energy to the shell and contents. An outlet tube with valve provides for filling the calorimeter or withdrawing vapor. Detachable receivers, suitable for weighing are connected to the outlet tube to hold the samples of fluid transferred.

For confining the energy, the calorimeter is well insulated from external sources of heat, whereas in operation the temperature of an enveloping shell is kept close to that of the calorimeter shell. By observing the temperature differences periodically, the small amount of heat that leaks to or from the calorimeter can be accounted for.

In the vaporization measurements, the process is virtually isothermal. Heat is supplied to evaporate a sample of liquid that is withdrawn from the calorimeter at a controlled rate, col-

*Deceased.

[1] Figures in brackets indicate the literature references at the end of this paper.

lected by condensation, and weighed. It was shown by Osborne [1] that the heat put in per unit mass withdrawn is a characteristic quantity called gamma, γ, which is usually about equal to the latent heat of vaporization, L, for vaporization experiments performed below the normal boiling point. The difference between γ and L lies in the physical process. In a vaporization experiment in a calorimeter where the liquid is in equilibrium with its vapor, heat is supplied not only to vaporize the material withdrawn from the calorimeter, but also to vaporize material to fill up the space previously occupied by the material withdrawn from the calorimeter. This means that the quantity γ is always larger than L by this correction term, which is called beta, β. That is,

$$L=\gamma-\beta.$$

The quantity β has been shown to be

$$\beta=Lv/(v'-v)=Tv\,dp/dT,$$

where v and v' are specific volumes of saturated liquid and vapor, respectively, T absolute temperature, and dp/dT the vapor pressure derivative. In the present determinations β is so small that approximate evaluation is adequate for derivation of values of L.

In the heat capacity experiments, the calorimeter with a sample of fluid is heated over a measured temperature range. By making some experiments with different amounts of fluid, it is possible to account for the tare heat capacity of the calorimeter, and to obtain the change of a quantity denoted by alpha, α, which is a characteristic property of the fluid. The theory shows that the change in α differs from the change in enthalpy, H, of saturated liquid by the change in β, mentioned above. In algebraic form,

$$\Delta H/\Delta T=\Delta\alpha/\Delta T+\Delta\beta/\Delta T.$$

3. Apparatus

The essential features of the calorimeter may be explained by reference to figure 1. The metal calorimeter shell, C, provided with an electric heater, H, is supported within an insulating space and is surrounded by a thermal guard shell or envelope, E, for control of heat leak. Provision is made for transfer of a fluid sample between the fluid container, FC, and the calorimeter, C, by

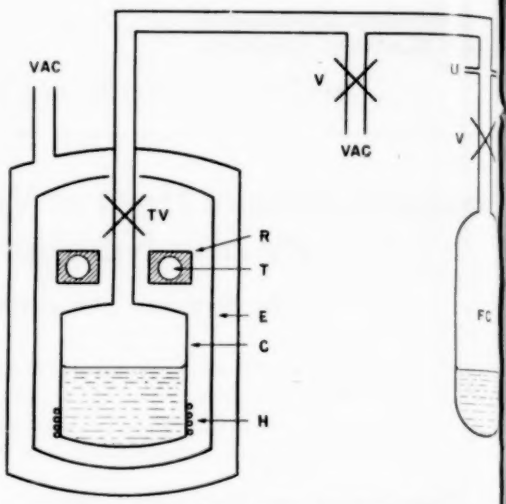

FIGURE 1. *Schematic drawing of apparatus.*

C, Calorimeter shell; *E*, envelope; *FC*, fluid container; *H*, calorime heater; *R*, reference block; *T*, resistance thermometer; *TV*, throttle va *U*, union; *V*, valve.

distillation through the throttle valve, *TV*. Th calorimeter shell and envelope are enclosed with an outer shell with an outlet tube used for bot evacuation and electric leads. The space with this outer shell, and the calorimeter and its co nections may be evacuated through connection *VAC*. The copper reference block, *R*, is in region of uniformly controlled temperature an provides a thermal connection between two plat num resistance thermometers, *T*, and the referenc junctions of thermoelements used for measurin the temperatures of points on the calorimeter she and envelope. In use, the outer shell of this cal rimeter unit was immersed in a water bath fo control of surrounding temperature. The cal rimeter and essential parts are shown in mos detail in figure 2.

(a) Calorimeter Shell and Included Parts

The calorimeter shell shown at C, figure 2 is double-walled unit. The inner shell serves as container for the fluid sample. The outer shell attached to the periphery of the inner shell at *A* is a thermal shield that gives the calorimeter nearly isothermal surface regardless of tempera ture gradients in the shell of the fluid containe This outer shell is made of copper 0.1 mm thick The inner shell is made of brass with a cylindrica section 0.5 mm thick and with rounded endcaps

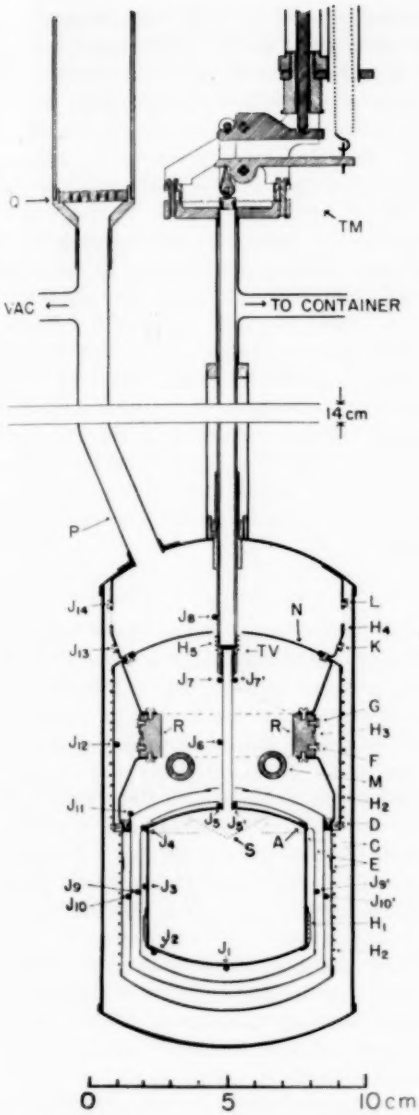

FIGURE 2. *Scale drawing of calorimeter.*

A, Attachment of calorimeter shell to its shield; *C*, calorimeter shell and shield; *D*, attachment of envelope to its shield; *E*, envelope and shield; *F*, *G*, *K*, *L*, zones of thermal attachment of thermoelements; H_1, calorimeter heater; H_2, envelope heater; H_3, reference block heater; H_4, heater; H_5, throttle valve heater; J_1, J_2, etc., thermoelement measuring junctions; *M*, resistance thermometer receptacles; *N*, envelope deck; *P*, lead-wire duct; *Q*, seal for electrical leads; *R*, reference block; *S*, gauze baffle; *TM*, throttle valve mechanism; *TV*, throttle valve seat.

This shell is put together with soft solder, the end caps fitting into shallow recesses in the ends of the cylinder that are spun down over the caps for strength. The outer surface of the inner shell and both surfaces of the outer shell are gold-plated and polished to minimize heat transfer by radiation. Heat transfer between these shells by gaseous conduction is essentially eliminated by evacuation.

The calorimeter heater, H_1, is a 100-ohm resistor of No. 34 constantan wire, insulated with fiber glass and wound over a strip of thin mica cemented to the brass shell by glyptal lacquer. On top of this winding is cemented another thin mica strip covered by a copper sheath, which is spun down on both sides of the winding and soldered to the brass shell. This sheath not only presses the heater element into good thermal contact with the brass shell but also conducts back to the brass shell the heat that it receives from the heater. Leads of 0.4-mm copper wire insulated with enamel and silk are brought out from the copper sheath between mica strips.

In the interior of the calorimeter shell there was a cellular system of copper, for the purpose of promoting the rapid distribution of heat. This tends to avoid excessive thermal gradients and lag of temperature equalization. This heat distributing system consists of vertical sheets of copper (0.1 mm thick) arranged as shown in the cross section figure 3. There are 30 sheets of tin-coated copper cut to shape and bent so that, when spaced and attached by tin solder to the inner surface of the brass cylinder, they form 60 radial plates, 30 of which extend to the central void of 5-mm diameter, and 30 more that extend to a diameter of 25 mm. At the bottom these plates extend close to the bottom cap, whereas at the top they extend only to the level of the top joint, leaving a small open space under the top cap. With this system of plates, no part of the liquid sample in the calorimeter is more remote than about 3 mm from a conducting metal part.

Directly on the level top of the copper plates is a baffle (*S*) of silver wire gauze, 100 mesh to the inch, in the form of a ring extending to the outer cylindrical wall and cut out at center to 24-mm diameter, and spaced to allow free flow of vapor upward in the center. Another baffle of conical shape rests with vertex at center and base against the top cap at a diameter of about 3 cm. At this perimeter, four spaces are left for vapor flow in toward the outflow tube in center of top cap. The purpose of these two baffles is to intercept any drops of liquid that might be projected directly

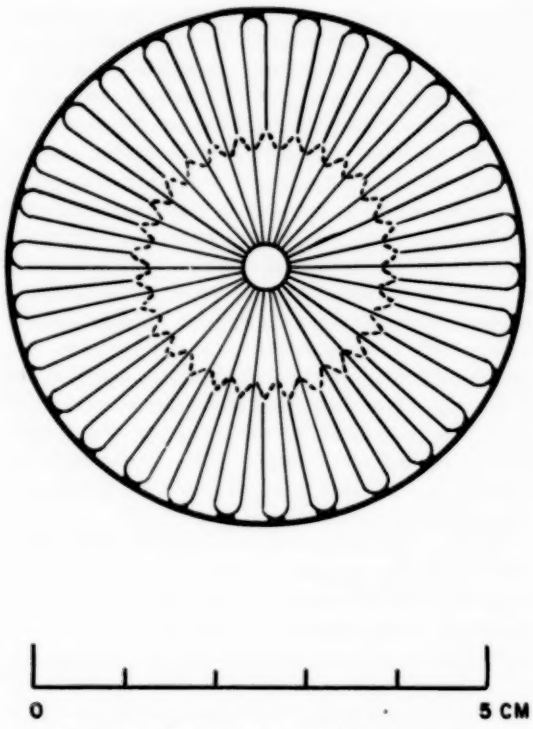

FIGURE 3. *Calorimeter heat distributing system.*

into the vapor outflow tube by active boiling, should it occur. They also probably favor the tempering of the vapor to the temperature of the top part of the calorimeter.

(b) Thermal-Protecting Enclosure

The three obvious and familiar means for avoiding the gain or loss of unmeasured heat were provided by use of a protecting enclosure for the calorimeter. These three means are thermal insulation, thermal control of envelope, and temperature-survey provision.

Thermal insulation was provided by evacuation of the space between calorimeter wall and envelope wall, and by gold plating and polishing the wall surfaces to give low emissivity. Furthermore, the unavoidable solid connections between the two elements such as electric lead wires were kept to tolerable proportions.

Thermal control of the envelope was effected by an electric heater, H_2, on the outer wall of the double-walled envelope, and by survey thermoelements for observing the temperature differences. The actual control was effected either manually by an observer of the thermoelement indications or by the automatic means to be described later. The inner guard wall of the envelope was made similar to the outer-shield wall of the calorimeter so that residual thermal gradients in the opposed heat-leak surfaces would be alike and compensate each other.

From the periphery of the envelope at D, a cylindrical extension with heater H_2 and cap, N, provided for a thermally controlled space suitable for the reference block, R, and also for the outflow tube, and throttle valve, TV. The calorimeter shell (that part of the apparatus containing the sample of hydrocarbon) is supported by the outflow tube, which is attached to the center of the outer cap. This tube passes without contact through the envelope and through the cap, N, which is the upper boundary of the protecting enclosure.

(c) Vapor Line and Throttle Valve

The section of the outflow tube between the calorimeter and the seat of the throttle valve was of stainless steel (8 Ni—18 Cr), having an inside diameter of 3.5 mm and a wall thickness of 0.25 mm. The top of this steel tube was left thicker and was machined in the form of a circular rim, sharply beveled to about a 90-degree angle. This beveled rim formed the seat of the throttle valve, which was closed or opened by the seating or withdrawal of the valve stem end. This consisted of a thin coating of tin on a flat silver disk normal to the axis of the valve stem.

Motion of the valve stem through the tubular stem casing of copper-nickel was controlled by a specially designed mechanism. This mechanism is the identical one previously used in apparatus for measurements on water [4].

The essential difference between the previous valve assembly and the present one is the increased length of the valve stem. In the present design, intended to be useful at subatmospheric temperatures and within an evacuated space, the length was increased to about 30 cm by using a section of copper-nickel tube of 5.3 mm outside diameter and 0.3 mm wall thickness, as an extension. The ends of this tubular section were formed by pressing into a triangular fluting or Y shape. For the purpose of exact centering of the stem on its seat, the lower fluted section was lathe turned to

a slip fit in the section of the tubular sleeve just above the valve seat. The end was recessed to receive the silver disk for the stem end. At the top end a brass bushing was fitted to engage the male thread of a stud extending through the diaphragm. In order to utilize the inside of the tubular stem as flow space, the tube was perforated at each end by three holes where the Y section joined the circular part.

A heating coil, shown at H_5 in figure 2, was wound directly on the casing of the throttle valve to permit control of the temperature of the valve and outlet tube. The purpose of this control was to avoid error due to condensation.

The outlet tube extends vertically up from the valve and out horizontally from the diaphragm cell. From there it leads through a metal tube to a glass stopcock, beyond which a metal union provides for the attachment of one of several Pyrex-glass containers for holding a sample of fluid. A side tube permits evacuation of the vapor line. The glass containers of about 225 ml capacity are provided with unions and stopcocks so that they can be detached and weighed for determining the amounts of samples.

(d) Thermometric Installation and Other Wiring

Platinum resistance thermometers supplemented by thermoelements were used in the control and measurement of temperatures. Two resistance thermometers placed at M in the copper reference block determined a reference datum on the International Temperature Scale, from which small temperature differences to the calorimeter shell or other points were measured by means of thermoelements. Thermoelements were also used differentially for the survey of temperature distribution and for the regulation of the calorimetric processes.

The advantages of this combination of resistance thermometers and thermoelements in calorimetry have been recognized and used in this laboratory for a quarter of a century. The reliability of the modern platinum-resistance thermometer to reproduce the International Temperature Scale justifies its use to establish the reference datum of temperature. On the other hand, thermoelements are quite sufficient for supplementing resistance thermometers in the measurement of small temperature differences, because uncertainties of calibration and inhomogeneities of wire introduce negligible errors in temperature determination. Furthermore, thermoelements have the advantages of lower heat capacity, better responsiveness, greater adaptability to limited space and to difficulty accessible points, and the possibility of multiple combinations to give integration of temperatures, more sensitivity, and measurement of temperature differences.

The use of a well-conducting, suitably shaped mass of metal as a reference block is a method of utilizing these virtues. The purpose of the reference block, besides furnishing a close thermal connection between the standard thermometer and the temperature measuring thermoelements, is also to bring all the reference junctions to a common temperature so that they may be used differentially. The increased precision and reliability gained by the use of a reference block outweighs the disadvantage of greater complexity of construction and of increased accessory equipment.

The reference block, R, was located in the space just above the calorimeter and envelope, where it was convenient for wiring. Here it was isolated from outer temperature differences so that its temperature was subject to precise control. This block was of copper in the form of a horizontal ring of rectangular section, to which were soldered two heavy-walled copper tubes, M, fitting in grooves cut in the lower face of the ring. These tubes served as resistance thermometer receptacles and were reamed to a free fit for the cylindrical platinum cases of the two resistance thermometers. A shallow groove was cut in the middle of the outer cylindrical face of the ring to receive a heating coil, H_3, for temperature control. The outer cylindrical face of the ring was used for attaching reference junctions of the thermoelements and also attachments for the leads to thermoelements and resistance thermometers. These attachments, besides fixing the wires in position, were for intercepting heat conducted along the leads and will be referred to as "tie-downs".

The two platinum-resistance thermometers, one of which was used as a working standard, and the other for a calibration check, were of the four-lead potential-therminal type described by C. H. Meyers [5]. The windings were of pure platinum wound on mica cross. The wire was 0.1 mm in diameter and was first wound into a helix of about 0.5 mm diameter before being wound in the

notched mica cross. The thermometers were encased in tubes of platinum of 6.35 mm outside diameter and about 0.2 mm thickness, which fitted closely into the receptacles in the reference block. The cases were lined with mica 0.01 mm thick to guard against possible electrical contact with the platinum wire.

The four lead wires were brought through holes in the shallow reentrant platinum cap, from which they were insulated by small beads of fused glass. The caps, which fitted closely into the casing, were welded to it in such a manner as to leave the outer surface clear for insertion into the receptacle, with only the leads projecting out. The opposite end of the thermometer case was spun down to a diameter of about 2.5 mm where a short section of glass tubing was fused on so that it could be filled with helium and sealed. The thermometers were annealed in air at about 475° C for about 8 hr.

The calibration was made in terms of the International Temperature Scale by using the fixed points of ice and steam and an intercomparison at 50° C with a primary standard resistance thermometer. The thermometers fulfilled the requirements of the International Scale and were selected from a group of four for their consistency. Each had a resistance of about 40 ohms at the ice point.

The 16 thermoelements were all wired with leads to the outside so that each thermoelement could be used either separately or in desirable combination. The positions of the measuring junctions are indicated in figure 2. The reference junctions of the thermoelements J_1 to J_{13}, inclusive, are located on the reference block (R in fig. 2). The thermoelements $J_{7'}$–$J_{5'}$ and $J_{10'}$–$J_{9'}$ are differential thermoelements with junctions only where indicated. The thermoelement J_{14} has its reference junction at J_{13} as noted later.

The group J_1 to J_5 in series was used to measure the average temperature of the calorimeter shell relative to the reference block when the calorimeter was in equilibrium at the beginning or end of an experiment. Simultaneous readings of the resistance thermometer in the reference block completed the temperature observation.

The thermoelements J_6, J_7, and J_8 were located on the vapor tube along which occurs all the heat leak by conduction to and from the calorimeter shell (all the electric leads were tied thermally to this vapor tube). The combination J_7 against J_5 was used to measure this heat leak, and another duplicate combination $J_{7'}$ against $J_{5'}$ was used for automatic regulation of this heat flow.

The thermoelements J_9 and J_{10} were located on the outer calorimeter shell and the inner envelope shell, respectively, and are used differentially to measure heat leak by radiation between these two surfaces. Heat leak by gaseous conduction and convection was eliminated by evacuation. A duplicate thermoelement combination, $J_{10'}$ against $J_{9'}$ was used to automatically regulate this radiant heat leak. These thermoelements were carefully located so that they indicated closely the average temperatures of their respective shells under all conditions. Temperature gradients in the shells had a negligible effect on any heat leak accounting.

The thermoelements J_{11}, J_{12}, and J_{13} were located on the upper part of the envelope shell and were observed in order to properly distribute the heat among the heaters on the envelope shell. The thermoelement J_{14} was located in thermal contact with the outer copper container and was different from the other thermoelements in that it had its reference junction at the temperature of J_{13} for reading the temperature difference between J_{14} and J_{13}. It was used in the regulation of the temperature of the bath surrounding the outer case.

The thermoelements used in this apparatus were made of No. 32 (0.20-mm) Chromel P wire containing about 90 percent of Ni and 10 percent of Cr, and No. 34 (0.16-mm) constantan wire containing about 60 percent of Cu and 40 percent of Ni. These wires, which gave about 60 μv per degree C for single elements, were insulated with silk and covered with Glyptal lacquer. The junctions of these elements were made in three different ways, depending on the way the thermal contact had to be made to acquire the temperature of the surface where they were placed.

The usual type of thermoelement junction was made on a small sheet of copper, either shaped as a circular washer with a radial tag, or as a rectangular terminal. The two wires to be joined were soldered close together to the terminal in the manner described in a previous report [3]. The rectangular type terminals were used for measuring junctions on the calorimeter and its envelope, and were attached thermally by inserting them between mica insulation and cementing with lacquer under small copper clips soldered to the surface. The washer-type terminals were

attached by clamping with screw studs and nuts between thin mica washers, either to the reference block or to the two tempering rings (yet to be described) that were installed for intercepting heat conducted from outside down the leads.

A third type of junction and attachment was used for junctions J_5, $J_{5'}$, J_6, J_7, $J_{7'}$ and J_8. In this type, the ends of the two wires were soldered together, and the wires reinsulated with silk, and bound and lacquered to the tube for several turns away from the junction to insure adequate thermal contact.

The thermometer leads were tied thermally to the reference block with the washer type of terminals anchoring the thermometer leads to the reference block and also at three additional zones, including the tempering rings.

Four horizontal zones of thermal attachment of thermoelements, thermometer leads and heater leads are designated in figure 2 as *F*, *G*, *K*, and *L*. Zones *F* and G were located on the reference block, and had 30 screw studs for thermal "tie-down" on each zone. Zone *K* was located on the copper tempering ring that was thermally integral with the upper cap of the envelope extension. This ring had a heater, H_4, for temperature control, and bore 40 thermal tie-downs. Zone *L* was another tempering ring that was thermally integral with the top cap of the outer shell. This also had 40 thermal tie-downs.

Four mica struts formed the supporting attachment between ring *K* and ring *L*, and these struts carried the entire envelope structure rigidly, with negligible heat transfer.

The reference block was carried between eight copper-nickel legs, four above and four below. These legs were 0.8 mm thick and 3.4 mm wide, and formed a near-rigid support for the envelope shell below. The envelope extension above *D* could be lowered for access to the wiring space about the reference block. The wires leading from the reference block, zone *G*, to the tempering ring, zone *K*, passed through slots in the outer rim of the cap.

Leading from the tie-downs on the tempering ring, zone *K*, the wires passed through the gap between the two rings *K* and *L*, and thence out through the lead-wire duct, *P*. Within this duct the wires, including thermoelements, thermometer, and heater leads were grouped into compact bundles with heater leads separate from the others to lessen danger of electric leakage. At the top of this duct the wires passed out through small holes in a lucite cap, *Q*, that was sealed with a resin lacquer, so the entire interior space could be evacuated through the side tube from the lead duct.

The system of several zones of tie-downs for the various electrical lead wires was designed to intercept heat leak along these wires to protect the thermometric elements from extraneous lead conduction effects. The small thermal conduction along the electrical leads from the calorimeter shell was accounted for by tieing them thermally to the vapor line between thermoelements J_7 and J_5, and including their conduction with the metal tube conduction as measured by J_7 against J_5.

Outside the calorimeter the leads were brought over to the observing station where specially built all-copper selector switches provided for various combinations of thermoelements for the several functions mentioned above. By manipulation of these switches, the observer could quickly shift from one combination to another with delay only for galvanometer response.

The emf's of the thermoelements were measured on a Wenner potentiometer. The errors of both the potentiometer and the thermoelements were inconsequential for this purpose.

The five thermoelements, J_1 to J_5, used to measure the temperature of the calorimeter shell, were calibrated in place by comparison with the resistance thermometer in the reference block. This procedure was first to observe the thermometer and thermoelements, when the reference block temperature was very close to that of the calorimeter. The reference block was then heated for a few seconds, while the calorimeter temperature remained virtually constant, and the observations were repeated. The change in emf of the thermoelements was thus given in terms of the temperature scale. No evidence was found that the calibration factor of any of the other similar thermoelements differed from this one, but even had they differed, the manner of use avoided any significant error due to this cause as the heat leak factors were experimentally determined, and the thermoelement readings were calibrated directly in terms of power.

The resistances of the two platinum thermometers were measured with a Mueller bridge [6] and were calibrated previous to their installation

in the reference block. Intercomparisons of the two thermometers made at several times during the progress of the measurements showed that no significant relative change had occurred. Small changes in the thermometers would have caused only insignificant effects on the calorimetric results.

Use of a commutator with normal (N) and reverse (R) positions adapts the bridge for measuring the resistance thermometer. A bridge current of 0.005 amp was used, half of which passed through the thermometer. A reversing snap switch for the bridge current served both to account for galvanometer zero drift and also to double the sensitivity.

(e) Auxiliary Control Features

One very important control feature has already been described, i. e. the vapor throttle valve. This is adjusted manually by the operator to open or shut the vapor line and to regulate the evaporation temperature.

Other control devices are used in the various heating circuits some of which are manual, some automatic, and some partly each. One of the latter type is the main switch in the calorimeter heater circuit. This is a double-pole double-throw switch, which is thrown either way by a spring tensed by a hand lever. The switch is released for quick throw by a trigger pulled by the electric seconds signal from the standard clock. A key in the clock circuit allows the operator to choose the particular second signal to start or stop the calorimeter heating current. The heating periods are normally integral numbers of minutes.

The heating circuits for control of the temperatures of the envelope and envelope extension were divided into two entirely separate parts. One of these circuits served to supply the additional heat required during a heat capacity experiment. This heater circuit was arranged to distribute the heat according to the heat capacity of the envelope and envelope extension and was used only during a heat capacity experiment. No adjustment of the current in this heater circuit was necessary due to the use of the second heater circuit. The second heater circuit served to supply the heat lost to the surroundings from the envelope and envelope extension and was arranged to distribute heat to account for different heat transfer coefficients in different regions. This second heater circuit was operated by an automatic control at all times. By using these two heater circuits it was possible to avoid large gradients on the envelope and envelope extension during a heat capacity experiment, and still utilize automatic control.

The automatic control was actuated by the emf of thermoelements $J_{10'}-J_{9'}$, previously indicated. This emf in a simple potentiometer circuit actuated a galvanometer, photoelectric cell and amplifier, which continuously regulated the heating current to control the temperature difference. The temperature gradient along the vapor tube was automatically regulated to a desired value by a similar circuit actuated by the emf of thermoelements $J_{7'}-J_{8'}$. Each heater is connected directly in the plate circuit of two type-25L6 electron tubes in parallel, which were in turn driven by type-38 electron tubes that were controlled by the photoelectric cell-galvanometer combination. The advantage of this system was that the control of the current in the heaters was continuous instead of on-and-off. The automatic controls regulated the temperature of the envelope and throttle at any desired temperature difference from the calorimeter even when changes occurred in the temperature of the calorimeter, such as during heat capacity experiments.

The heating coil on the reference block and the one used in the water bath are both manually controlled.

(f) Measurement of Mass and Electric Energy

A sensitive balance of a capacity of 2 kg with closed cabinet below in which containers, dummies, and counterpoises were suspended, was used for weighing the samples. Calibrated platinum-plated brass weights were used.

A Wolff-Diesselhorst potentiometer was used for measurements of current and potential drop in the calorimeter heater. These data with time intervals furnished by a Rieffler standard clock determined the electric energy. A 0.1-ohm four-terminal resistor in series with the heater was used for the current measurement and a 1,000 to 1 ratio volt box was used for the potential drop. The potential drop was measured by two leads that join the current leads at the zone K (fig. 2). The heat developed in the current leads between the calorimeter shell and the potential leads was accounted for by calculation, knowing the resist-

ce of the leads and assuming an arbitrary calorimeter boundary near thermoelement J_6. This correction was estimated as 0.027 percent and was believed to introduce no significant uncertainty in the results. If the calorimeter boundary had been taken at J_7 or J_5, instead of at J_6, the maximum difference in the correction would have been only 0.006 percent.

All the important electrical-measuring instruments were carefully calibrated.

4. General Evaluation of the Calorimeter

The calorimeter was designed mainly for measuring heats of vaporization of small amounts of hydrocarbons, and incidentally for measuring liquid heat capacities. It was found possible to make accurate measurements of the heat of vaporization with only a few grams of material. In other words, the vaporization experiments could proceed until the calorimeter was practically dry. This was made possible by the effective heat distributing system in the calorimeter and the isothermal shields on the calorimeter and envelope that made heat leak evaluation essentially independent of any temperature gradients on the calorimeter shell or on the envelope. The electronic automatic controls on the envelope and throttle temperatures, effective in all types of experiments, were a great help in the manipulation of the apparatus. The fact that vaporization experiments were made with a large number of hydrocarbons is evidence of the ease of operation of the apparatus. After a little experience, it was found possible to dry a sample of hydrocarbon, free it from air, distill it into the calorimeter, make several vaporization experiments, and empty the calorimeter, all in a normal working day.

II. Heat of Vaporization of 59 Hydrocarbons

1. Introduction

Measurements of heats of combustion of hydrocarbons are used in the determination of heats of formation of the hydrocarbons which, in turn, are used to calculate heats of reaction and equilibrium constants involving hydrocarbons. Combustion experiments usually start with the hydrocarbon in the liquid state so that knowledge of the heat of vaporization is necessary to obtain heats of formation. The calorimetric apparatus described in section I was constructed for the purpose of accurately measuring heats of vaporization of a number of samples of pure hydrocarbons that had become available.

2. Method

In the vaporization experiments, the measured heat was supplied electrically to evaporate liquid, while vapor was withdrawn at a rate that was controlled manually to keep a constant temperature of evaporation. According to the theory of fluid calorimetry [1], the energy added per unit mass removed as vapor, designated as gamma, γ, exceeds the latent heat of vaporization, L, by the quantity beta, β.

$$L=\gamma-\beta,$$

where

$$\beta=Lv/(v'-v)=Tv\,dp/dT$$

where T is absolute temperature, p is the vapor pressure, and v and v' are the specific volumes of liquid and vapor, respectively.

3. Preparation of Samples

All of the hydrocarbons used in the present investigation were obtained in 1941 and 1942 from the NBS Section on Thermochemistry and Hydrocarbons through Frederick D. Rossini. The various samples are identified as follows: *n*-Pentane, *n*-hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, *n*-heptane, 2,2-dimethylpentane, 3,3-dimethylpentane, 2,2-dimethylhexane, 2,3-dimethylhexane, 3,3-dimethylhexane, 2-methyl-3-ethylpentane, 3-methyl-3-ethylpentane, 2,2,3-trimethylpentane, 2,2,4-trimethylpentane, 2,3,3-trimethylpentane, *n*-nonane, *n*-decane, methylcyclopentane, methylcyclohexane, *n*-propylcyclohexane, *cis*-1,2-dimethylcyclohexane, *trans*-1,2-dimethylcyclohexane, *cis*-1,3-dimethylcyclohexane, *trans*-1,3-dimethylcyclohexane, *cis*-1,4-dimethylcyclohexane, *trans*-1,4-dimethylcyclohexane, benzene, toluene, ethylbenzene (first sample), *m*-xylene, *n*-propylbenzene, and isopropylbenzene, were samples from the same lots the purification and properties of which were later reported by Forziati, Glasgow, Willingham, and Rossini [7].

n-Octane, 2-methylheptane, 3-methylheptane, 4-methylheptane, 3-ethylhexane, 2,4-dimethylhex-

ane, 2,5-dimethylhexane, 3,4-dimethylhexane, 2,3,4-trimethylpentane, *n*-propylcyclopentane isopropylcyclopentane, cyclohexane, ethylcyclohexane, *o*-xylene, and *p*-xylene were samples prepared by C. E. Boord and collaborators on the American Petroleum Institute Hydrocarbon Research Project (now the American Petroleum Institute Research Project 45) at the Ohio State University.

2,3-Dimethylpentane (both samples), 2,4-dimethylpentane, 3-ethylpentane, 2,2,5-trimethylhexane, and 2,3,5-trimethylhexane were samples from the same lots, the purification and properties of which were later reported by Howard, Mears, Fookson, Pomerantz, and Brooks [8].

2,3-Dimethylbutane was from the material prepared by Cramer and Mulligan [9]. The second lot of ethylbenzene was from J. Timmermans [10]. 1,2,3-Trimethylbenzene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene were samples from the materials whose properties were described by Mair and Schicktanz [11].

2,2,3-Trimethylbutane and hexamethylethane were samples purified by the American Petroleum Institute Research Project 6 at the National Bureau of Standards from material supplied by George Calingaert, Ethyl Corporation, Detroit, Michigan [12].

In connection with the amounts of impurity (not including water) in the samples, and the effect of such impurities on the heat of vaporization, the following points may be noted: The manner of preparation and purification of the compounds was such as to leave as impurity only those substances having boiling points and other properties near those of the given substance. The amount of such impurity was less than 0.01 mole fraction for many of the compounds, between 0.01 and 0.03 mole fraction for some, and near 0.04 mole fraction for several. It is highly improbable, however, that any of the values of the heat of vaporization will be in error by more than 1 in 1,000 because of the small differences in the values of the heat of vaporization for those close-boiling isomers that might be expected to be present in one another as impurities. For most of the compounds, it appears that the error from these impurities will not exceed 1 in 2,000 and for some the error from this source will not exceed 1 in 10,000.

It was necessary to remove both air and a trace of water from the hydrocarbons before making calorimetric measurements on them. The a was effectively removed by distillation into cold trap from which the air was continual removed by pumping. The trap was immers in a solid carbon dioxide-ethanol bath so th there was negligible loss of the sample. A seco distillation from the trap to the detachable co tainer indicated that essentially all of the a had been removed.

The water was usually removed from the hydr carbons by running the liquid hydrocarbo slowly through a tube packed with silica gel, an into the evacuated container from which the fir distillation was made. Tetraethylene citrate w used as a stopcock lubricant because it was n affected by the hydrocarbon.

As traces of water were visible as ice in th cold hydrocarbon even after this drying pro cedure, it was necessary to measure the effectiv ness of the drying. The sample of toluene samp was prepared in the usual manner and used i the calorimeter in the vaporization experiment Upon completion of these experiments, the toluen was distilled to a bulb where the water conte was measured by a method similar to that use by Aldrich [13] at this Bureau in the determin tion of water in gasolines. A liquid alloy sodium-potassium was added to the hydrocarbo and agitated until all of the water had reacte The pressure of the hydrogen evolved was mea ured after the hydrocarbon had been frozen wit liquid air. From this pressure, and the volum and temperature of the system, the water conte was calculated to be less than one part in 25,00 in the sample. This would affect the measure heat of vaporization of the toluene by less tha 1 part in 5,000. It is believed that the error du to water present was never more than this amoun in any of the hydrocarbons, and was usuall much less.

Other experiments were performed to obtai additional evidence on the adequacy of the dry ing. In addition to the drying with silica ge some experiments were made in which the wate was removed by cooling the sample to solid car bon dioxide temperatures and filtering out th traces of ice with fiber glass. Other experiment were made in which the samples were dried wit P_2O_5. All of these experiments indicated tha the drying of the hydrocarbons with silica g was sufficiently effective.

4. Experimental Procedure

Accounting for Mass, Energy, and Change in State of the Sample

The mass of fluid withdrawn as vapor enters as a direct factor in the reduction of the data, and therefore the results can be no more reliable than the determinations of these masses. Special care was taken therefore to avoid both systematic or accidental error in the weighings. For each weighing, an account was kept of the amount in the calorimeter at any time and a final mass check made by completely exhausting and weighing the residual after a series of experiments.

The amount of fluid evaporated and collected by condensation was seldom less than 10 g in a single experiment, although occasionally when the supply was limited, smaller portions were taken.

In order that the weighings be made with suitable precision, the glass containers holding the condensed samples were given a routine treatment of preliminary conditioning. The container, holding a sample that had been collected by condensation in a cold bath of dry ice and alcohol, was warmed to the temperature of the room. The container was then wiped dry with a towel, dried further in front of a fan, and then hung in the balance case for at least 30 minutes to assume a steady temperature. Weighings were then made by substitution, estimating to 0.1 mg by reading swings. A dummy glass container was kept in the balance case and was weighed either just before or after the sample, to eliminate errors of weighing due to accidental changes in the balance or the counterpoise. The weights were corrected for buoyancy in air.

Measured energy was supplied electrically to the calorimeter and its contents by means of the heating coil installed on the sample container as described in section I. Power was supplied by a separate storage battery of large current capacity. Potentiometer readings were made periodically for obtaining the energy added electrically, as described later.

In order to avoid a large initial change when the current was switched to the calorimeter heater at the start of an experiment, a substitute resistor, equal to the calorimeter heater resistance, was used to adjust and steady the battery output. Between experiments, the current in the substitute was adjusted to the value selected to give the desired evaporation rate in the next experiment.

The means provided for the control and evaluation of heat leak have been described in section I. In operation, there were usually small deviations from the ideal control that would have annulled heat leak. The small corrections for this remaining heat leak were evaluated with the aid of the differential thermoelements. The indicated differences were observed every minute and added algebraically to give sums in temperature-time units called "heat-leak factors." These factors, when multiplied by "heat-leak coefficients," gave the heat-leak corrections for the energy in the individual experiments. The calorimeter was designed to make the coefficients small both by construction and by evacuation of the insulating space, and the manipulation of the envelope control was such as to make the factors small.

The heat-leak coefficients were determined experimentally during the early part of the program and were checked later. This was done by separate blank experiments with no electrical heat-input to the calorimeter and with no vapor withdrawal. The temperature difference between the calorimeter and envelope was held at a large measured value for a chosen time, yielding an exaggerated heat-leak factor. The envelope heat-leak coefficient was calculated from the energy change of the calorimeter and its contents, where this energy change was computed from initial and final calorimeter temperatures and the heat capacity of the calorimeter. Similarly, the tube heat-leak coefficient was determined in an experiment with an exaggerated tube heat-leak factor.

The correction for heat leak usually consisted of three parts, designated as "envelope," "tube," and "residual" heat leaks. The envelope heat leak was usually small because of the adjustment of the automatic control. The tube heat leak was purposely allowed to be larger in order to permit the temperature of the throttle and upper part of the vapor tube to run high enough to avoid condensation in the outflow tube. During the actual withdrawal of vapor, the tube heat leak was shown to be negligible, as the vapor flow controlled the temperature of the tube where it joined the calorimeter shell.

The residual heat leak was that which was not accounted for by the routine envelope and tube heat-leak determinations, because of possible devi-

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ations of the heat-leak coefficients from the values measure. This residual heat leak was accounted for by making frequent blank experiments while the calorimeter was in equilibrium between evaporation experiments. In these, both envelope and tube heat leaks were kept normal and accounted for, leaving the deviation of the energy accounting to give a rate of leak per unit of time, which if of significant amount, could be applied to the preceding experiment as a supercorrection.

The temperature of the calorimeter and contents, when in equilibrium, was measured by a resistance thermometer in conjunction with thermoelements, as previously described. The temperature change of the calorimeter and contents was thus always accurately observed in all experiments. All temperatures were finally expressed on the International Temperature Scale.

For determining either the initial or final temperature, each temperature observation consisted of simultaneous readings of the resistance thermometer and thermoelements. The five thermoelements J_1–J_5, in series, indicated the mean temperature of the calorimeter with respect to the reference block. Four successive temperature readings were made at half-minute intervals, from which the mean temperature was computed.

The temperature at which evaporation proceeded is of some importance, as the heat of vaporization varies with temperature. This was controlled by the operator to keep it as near as possible to the initial temperature. Thermoelement J_5 was taken as the guide for this control. Previous experience [4] together with surveys of the temperature distribution on the calorimeter shell during evaporation indicated that this point represented the best approximation to the temperature of the vapor as it left the calorimeter.

(b) Description of Vaporization Experiments

In preparation for a series of experiments on a sample, the calorimeter and vapor line were cleared of air by evacuation. The sample, prepared as previously described, was transferred from the glass container to the calorimeter by distillation. To do this, ice was packed around the calorimeter, and necessary heat was supplied to the container to evaporate the liquid. In this preliminary charging, the insulating space was filled with helium to increase the rate of heat flow from the calorimeter. For some of the samples of hig boiling points, the available pressure differen was so small that it required a long time for t transfer.

After the sample was transferred, the conta was reweighed and the calorimeter was heated the temperature of measurement, usually 25°, keeping the valve and tube at a temperature ab that of the calorimeter to avoid condensation the tube. Before starting the experiment, t insulating space outside the calorimeter w evacuated to provide the insulation. A weigh glass container was attached and the line evacua to the throttle valve. The container was ope to the line and the apparatus was then ready start the experiment.

The initial equilibrium temperature of t calorimeter and contents was observed first. the beginning of a chosen minute the current w switched from the substitute resistor to t calorimeter heater by the automatic time-tripp switch. The throttle valve was then opened the operator who was also observing the therm elements. The valve was adjusted continuou so as to keep J_5 at zero. The reference block w kept at a constant temperature as shown by t resistance thermometer. The upper part of t calorimeter, which followed closely the evapor tion temperature, was maintained at the init reference block temperature by regulating t vapor flow through the valve to just balance t energy added to the calorimeter. During t evaporation period the lower part of the calori eter in contact with the liquid became warmer b the amount of superheating necessary to condu the heat to the surface for evaporation.

To evaluate the heat-leak factors, the diffe ential thermoelements, J_9–J_{10}, and J_7–J_5, we observed at 1-minute intervals. The constancy the reference-block temperature was frequent checked to furnish a steady zero for therm element J_5, used to guide the regulation of t evaporation temperature. Occasional surveys all thermoelements were made to indicate a irregularities in behavior. The current and po tential drop in the calorimeter heater we observed on alternate minutes, starting one ha minute after the power was switched on.

At the end of the chosen number of minutes, t current was switched back from the calorimete heater to the substitute resistor, making the tim

factor of the energy an integral number of minutes as determined by the standard clock. The throttle valve was kept open long enough after the power was switched off to bring the calorimeter and contents to final equilibrium temperature near the initial temperature, usually within 0.01° C. After a pause of 10 minutes for attaining equilibrium, the final temperature was observed. Following that observation, and while changing container and weighing a previous sample, a blank experiment was conducted to obtain the residual heat-leak factor, previously described.

On most of the samples, experiments were made at several rates of evaporation, usually between ¼ and 1 g per minute. Smaller rates than ¼ g a minute were also used when necessary either because of limitations on account of the fluid characteristics, or else because of the limited amount of sample. The practice of using different rates of evaporation was a precaution to test for some conceivable source of error.

This practice has been followed for the past 30 years as a check on the various preventive measures for avoiding liquid mixed with the vapor in evaporation experiments. During the experiments on water, these measures had been so effective that no case was ever found where this change of rate gave a positive test for wet steam, even over the range from the ice point to within 1 degree of the critical temperature. In spite of this experience, the test has been continued as a routine safeguard against erroneous evaluation of the state of the vapor.

In the present case, if spray projected upward from the evaporating surface had escaped capture by the baffles and had been withdrawn with the vapor, the measured energy per unit mass would have been too small. Furthermore, if the temperature of the vapor indicated by the observation of J_5 thermoelement had been in error, the effect of the error might depend on the rate of flow. Absence of any evidence of the rate effect on the resulting value of the heat of vaporization, may be taken as contributing to the reliability of the results as far as the state of the fluid is concerned. Here again, it must be confessed the test showed no evidence of liquid mixed with the vapor. The baffles evidently have done their bit. Further evidence of reliability, as distinguished from consistency, was furnished by the experiments on water with this calorimeter.

5. Results of Vaporization Experiments

The results of the vaporization experiments are given in chronological order in table 1. The values of net energy, given in column 6, include not only the electrical energy input, but also the energies due to the various heat leaks (envelope, tube, and residual), the correction for the change in temperature of the calorimeter between the beginning and the end of the experiment, and the correction for any deviation of the evaporation temperature from the desired even temperature (usually 25° C). These components of the net energy are not listed separately, because the corrections are so small. In an average experiment, the arithmetical sum of all the heat leak corrections amounts only to about 1 joule, whereas the other corrections are even less. This is the result of careful control of the temperature of the calorimeter and its surroundings at all times during an experiment.

TABLE 1. *Results of vaporization experiments*

WATER

Date	Temperature	Mass	Evaporation rate	Net energy	γ	Mean γ_{25}	B_{25}	L_{25}
	°C	g	g/minute	int. j	int. j/g	int. j/g	int. j/g	int. j/g
11-8-41	25.0	9.8792	0.49	24113.5	2440.83			
Do	25.0	9.8929	.49	24144.1	2440.55			
11-10-41	25.0	20.2042	.51	49326.3	2441.39			
Do	25.0	10.1150	.51	24689.6	2440.89	2441.14	0.06	2441.08
Do	25.0	10.1164	.51	24694.0	2441.32			
Do	25.0	10.1181	.51	24699.3	2441.10			
11-12-41	25.0	9.8179	.49	23974.6	2441.93			

n-HEPTANE

11-21-41	25.0	9.7943	0.49	3573.83	364.89			
Do	25.0	9.8035	.49	3575.86	364.75			
Do	25.0	9.8061	.49	3577.23	364.80			
Do	25.0	9.8114	.49	3578.55	364.73	364.81	0.13	364.68
Do	25.0	14.7147	.49	5367.19	364.75			
11-26-41	25.0	9.8281	.49	3586.31	364.90			
Do	25.0	4.9249	.25	1796.56	364.79			
Do	25.0	19.8554	.99	7244.12	364.84			
Do	15.0	9.6531	.48	3580.46	370.91	.....	.....	.....
Do	35.0	9.9843	.50	3582.81	358.84	.....	.....	.....

2,2,4-TRIMETHYLPENTANE

12-8-41	25.0	11.6222	0.58	3575.88	307.68			
Do	25.0	11.4883	.57	3534.26	307.64	307.62	0.14	307.48
Do	25.0	17.0507	.57	5244.24	307.57			
Do	25.0	13.5587	.57	4170.72	307.60			

TABLE 1. *Results of vaporization experiments*—Continued

n-OCTANE

Date	Temperature	Mass	Evaporation rate	Net energy	γ	Mean γ_{23}	β_{23}	L_{23}
	°C	g	g/minute	int. j	int. j/g	int. j/g	int. j/g	int. j/g
12-16-41	25.0	9.9070	0.50	3597.96	363.17	363.16	0.05	363.11
Do	25.0	9.8089	.50	3594.77	363.15			
Do	25.0	11.8834	.50	4315.26	363.13			
Do	25.0	9.9041	.50	3596.89	363.17			

2-METHYLHEPTANE

1-2-42	25.0	10.4334	0.52	3624.17	347.36	347.37	0.07	347.30
Do	25.0	10.0047	.50	3474.39	347.28			
Do	25.0	9.9425	.50	3454.33	347.43			
Do	25.0	15.3498	.50	5332.69	347.41			

3-METHYLHEPTANE

1-8-42	25.0	9.9119	0.50	3455.64	348.64	348.72	0.06	348.66
Do	25.0	10.1243	.51	3530.14	348.68			
Do	25.0	10.5008	.52	3662.60	348.79			
Do	25.0	15.4967	.50	5405.06	348.79			

4-METHYLHEPTANE

1-14-42	25.0	10.1086	0.50	3511.86	347.41	347.34	0.06	347.28
Do	25.0	10.0087	.50	3475.75	347.27			
Do	25.0	10.0098	.50	3476.55	347.31			
Do	25.0	16.0145	.50	5563.06	347.38			

2,5-DIMEHTYLHEXANE

1-26-42	25.0	20.9621	0.52	6948.34	331.47	331.48	0.09	331.39
Do	25.0	22.1241	.50	7333.70	331.48			

n-NONANE

2-4-42	25.0	19.1859	0.48	6946.08	362.04	362.04	0.02	362.02
Do	25.0	20.0269	.50	7249.45	361.99			
Do	25.0	16.8176	.47	6089.36	362.08			

n-DECANE

2-11-42	25.0	4.6160	0.15	1665.79	360.87	360.97	0.01	360.96
Do	25.0	8.3058	.15	2999.02	361.08			
Do	25.0	7.0784	.15	2555.08	360.97			

2,3,4-TRIMETHYLPENTANE

2-16-42	25.0	9.7186	0.49	3208.08	330.10	330.14	0.08	330.06
Do	25.0	19.9360	.50	6582.39	330.18			

TABLE 1. *Results of vaporization experiments*—Continued

2,3,3-TRIMETHYLPENTANE

Date	Temperature	Mass	Evaporation rate	Net energy	γ	Mean γ_{23}	β_{23}	L_{23}
	°C	g	g/minute	int. j	int. j/g	int. j/g	int. j/g	int. j/g
2-20-42	25.0	9.8043	0.49	3192.19	325.59	325.83	0.07	325.76
Do	25.0	15.8101	1.58	5153.44	325.96			
Do	25.0	10.0081	0.50	3262.69	326.00			
Do	25.0	6.9949	.25	2278.50	325.74			
Do	25.0	9.7430	.49	3174.88	325.86			

WATER

2-25-42	45.0	6.3300	0.16	15156.6	2394.40			
2-26-42	25.0	10.2526	.51	25031.2	2441.45	2441.47	0.06	2441.6
Do	25.0	6.2581	.16	15278.6	2441.41			
Do	25.0	7.7441	.29	18906.6	2441.42			
Do	25.0	7.9806	.50	19485.4	2441.59			

3,3-DIMETHYLHEXANE

3-13-42	25.0	10.2026	0.51	3352.59	328.60	328.63	0.08	328.5
Do	25.0	25.0234	1.00	8223.19	328.62			
Do	25.0	8.0078	0.56	2631.99	328.68			
Do	25.0	10.0140	.50	3290.75	328.61			

2,3-DIMETHYLHEXANE

3-20-42	25.0	9.3631	0.47	3180.34	339.67	339.61	0.07	339.5
Do	25.0	18.5009	.97	6282.68	339.59			
Do	25.0	7.8080	.24	2650.99	339.52			
Do	25.0	11.1902	.49	3800.96	339.67			

2,2,3-TRIMETHYLPENTANE

3-23-42	25.0	8.0612	0.50	2606.23	323.30	323.20	0.08	323.12
Do	25.0	8.1525	1.02	2635.12	323.23			
Do	25.0	8.1516	0.26	2633.63	323.08			
Do	25.0	7.5364	.05	2435.74	323.20			

n-HEXANE

3-24-42	25.0	8.9398	0.45	3276.73	366.53	366.44	0.39	366.0
Do	25.0	14.5929	.91	5347.23	366.43			
Do	25.0	7.9004	.25	2894.89	366.42			
Do	25.0	10.8156	.49	3962.52	366.37			

2-METHYL-3-ETHYLPENTANE

3-26-42	25.0	9.7119	0.49	3275.51	337.27	337.25	0.07	337.18
Do	25.0	15.5975	.98	5259.28	337.19			
Do	25.0	7.6845	.24	2591.52	337.24			
Do	25.0	11.6749	.48	3938.02	337.31			

TABLE 1. *Results of vaporization experiments*—Continued

3-METHYL-3-ETHLYPENTANE

Date	Temperature	Mass	Evaporation rate	Net energy	γ	Mean γ_{25}	β_{25}	L_{25}
	°C	g	g/minute	int. j	int. j/g	int. j/g	int. j/g	int. j/g
4-27-42	25.0	9.9786	0.50	3319.54	332.67	332.59	0.06	332.53
Do	25.0	15.9652	1.00	5309.69	332.58			
Do	25.0	7.9748	0.25	2652.30	332.58			
Do	25.0	11.9768	.50	3982.73	332.54			

2,2-DIMETHYLHEXANE

4-30-42	25.0	9.0189	0.50	2945.01	326.54	326.49	0.09	326.40
Do	25.0	9.9168	.99	3237.56	326.48			
Do	25.0	7.9673	.25	2601.09	326.47			
Do	25.0	9.0576	.50	2957.02	326.47			

3-ETHYLHEXANE

4-31-42	25.0	9.4628	0.47	3284.57	347.11	347.07	0.06	347.01
Do	25.0	19.9138	.95	6911.25	347.06			
Do	25.0	7.5362	.24	2615.46	347.05			

METHYLCYCLOHEXANE

4-7-42	25.0	9.1250	0.46	3287.94	360.32	360.19	0.13	360.06
Do	25.0	11.9260	1.00	4295.67	360.19			
Do	25.0	19.9239	1.00	7175.15	360.13			
Do	25.0	9.9962	.50	3599.86	360.12			

CYCLOHEXANE

4-9-42	25.0	9.2557	0.46	3634.88	392.72	392.72	0.24	392.48
Do	25.0	29.6289	.99	11634.91	392.69			
Do	25.0	11.9967	.50	4711.61	392.74			

ETHYLCYCLOHEXANE

4-10-42	25.0	10.1008	0.50	3643.67	360.73	360.68	0.05	360.63
Do	25.0	27.5431	.98	9933.49	360.65			
Do	25.0	13.0929	.50	4722.00	360.65			

n-PROPYLCYCLOHEXANE

4-17-42	25.0	37.8146	0.51	13504.76	357.13	357.13	0.02	357.11

cis-1,2-DIMETHYLCYCLOHEXANE

4-20-42	25.0	14.4052	0.51	5098.87	353.96	353.92	0.06	353.86
Do	25.0	18.2952	.91	6475.32	353.94			
Do	25.0	15.5325	.51	5496.40	353.86			

TABLE 1. *Results of vaporization experiments*—Continued

trans-1,2-DIMETHYLCYCLOHEXANE

4-21-42	25.0	10.3778	0.52	3547.68	341.85	341.84	0.07	341.77
Do	25.0	30.0590	1.00	10274.63	341.82			
Do	25.0	10.0039	.50	3419.85	341.85			

trans-1,3-DIMETHYLCYCLOHEXANE [a]

4-22-42	25.0	9.7593	0.49	3409.64	349.37	349.34	0.07	349.27
Do	25.0	10.0295	1.00	3503.73	349.34			
Do	25.0	30.0092	1.00	10479.26	349.31			

cis-1,3-DIMETHYLCYCLOHEXANE [b]

4-24-42	25.0	10.0416	0.50	3421.84	340.77	340.70	0.08	340.62
Do	25.0	30.9169	1.03	10531.87	340.65			
Do	25.0	10.0596	.50	3427.22	340.69			

cis-1,4-DIMETHYLCYCLOHEXANE

4-27-42	25.0	9.8297	0.49	3419.41	347.86	347.84	0.07	347.77
Do	25.0	29.4440	.98	10241.26	347.83			
Do	25.0	9.8533	.49	3427.38	347.84			

2,3-DIMETHYLPENTANE (IMPURE)

4-28-42	25.0	11.7759	0.56	4027.50	342.01	342.10	0.13	(341.97) [c]
Do	25.0	10.0438	1.00	3436.17	342.12			
Do	25.0	9.9292	.50	3397.54	342.18			

2,3-DIMETHYLPENTANE (PURE)

4-29-42	25.0	10.1601	0.51	3472.74	341.80	341.77	0.13	341.64
Do	25.0	10.1885	1.02	3482.06	341.76			
Do	25.0	16.0369	0.30	3430.10	341.75			

3,3-DIMETHYLPENTANE

4-29-42	25.0	7.7358	0.52	2550.61	329.72	329.70	0.20	329.50
Do	25.0	6.1893	.52	2040.40	329.67			

2,2-DIMETHYLPENTANE

4-30-42	25.0	10.5002	0.52	3400.38	323.84	323.82	0.27	323.55
Do	25.0	10.4958	.52	3398.44	323.79			

[a] This isomer, formerly labeled "*cis*", has the following properties: boiling point at 1 atm., 124.45° C; refractive index, n_DS at 25° C, 1.4284; density, at 25° C, 0.7806 g/ml.

[b] This isomer, formerly labeled "*trans*", has the following properties: boiling point at 1 atm., 120.09° C; refractive index, n_DS at 25° C, 1.4206; density at 25° C, 0.7620 g/ml.

[c] Sample of lower purity.

TABLE 1. *Results of vaporization experiments*—Continued

2,2-DIMETHYLBUTANE (SILICA GEL DRYING)

Date	Temperature	Mass	Evaporation rate	Net energy	γ	Mean γ_{23}	β_{23}	L_{23}
	°C	g	g/minute	int. j	int. j/g	int. j/g	int. j/g	int. j/g
5-1-42...	25.0	10.5637	0.53	3401.41	321.99			
Do....	25.0	20.4006	1.02	6567.58	321.93	321.94	0.69	321.25
Do....	25.0	10.1914	0.51	3280.59	321.90			

2,2-DIMETHYLBUTANE (FREEZE OUT WATER)

5-8-42...	25.0	10.5422	0.53	3391.52	321.71			
Do....	25.0	15.3726	1.02	4949.10	321.94	321.93	0.69	321.24
Do....	25.0	10.2099	0.51	3288.96	322.14			

P_2O_5 DRYING

5-20-42...	25.0	10.0734	0.50	3243.28	321.96			
Do....	25.0	20.4435	1.02	6580.97	321.91	321.96	0.69	321.27
Do....	25.0	10.0818	0.50	3246.24	321.99			

N-PENTANE

5-14-42...	25.0	9.8235	0.45	3610.02	367.49			
Do....	25.0	14.3765	.90	5282.25	367.42	367.44	1.22	366.22
Do....	25.0	9.8489	.45	3618.69	367.42			

2,2,3-TRIMETHYLBUTANE

5-15-42...	25.0	10.1184	0.50	3236.38	319.85			
Do....	25.0	14.3947	1.03	4606.24	320.00	319.94	0.24	319.70
Do....	25.0	10.1393	0.51	3244.22	319.96			

trans-1,4-DIMETHYLCYCLOHEXANE (SILICA GEL DRYING)

5-18-42...	25.0	9.6050	0.48	3242.61	337.60			
Do....	25.0	23.5953	.48	7963.61	337.51	337.56	0.08	337.48

P_2O_5 DRYING

5-21-42...	25.0	9.6064	0.48	3244.39	337.73			
Do....	25.0	19.4755	.97	6573.17	337.51	337.58	0.08	337.50
Do....	25.0	9.6463	.48	3256.04	337.54			

2-METHYLPENTANE

5-26-42...	25.0	9.3458	0.47	3243.65	347.07			
Do....	25.0	18.9801	.95	6589.01	346.99	347.10	0.57	346.53
Do....	25.0	9.3494	.47	3246.47	347.24			

3-METHYLPENTANE

5-27-42...	25.0	9.6878	0.48	3406.42	351.62			
Do....	25.0	19.2642	.96	6775.16	351.70	351.68	0.45	351.23
Do....	25.0	10.0978	.50	3551.57	351.72			

TABLE 1. *Results of vaporization experiments*—Continued

METHYLCYCLOPENTANE

Date	Temperature	Mass	Evaporation rate	Net energy	γ	Mean γ_{23}	β_{23}	L_{23}
	°C	g	g/minute	int. j	int j/g	int. j/g	int. j/g	int. j/g
5-28-42...	25.0	9.4348	0.47	3549.01	376.16			
Do....	25.0	18.9391	.95	7123.43	376.12	376.12	0.34	375.8
Do....	25.0	9.4495	.47	3553.84	376.09			

n-PROPYLCYCLOPENTANE

5-29-42...	25.0	9.9500	0.50	3643.93	366.22			
Do....	25.0	13.7873	1.00	5047.64	366.11	366.17	0.05	366.12

ISOPROPYLCYCLOPENTANE

6-1-42...	25.0	8.3058	0.52	2920.95	351.68			
Do....	25.0	8.2092	1.02	2886.39	351.60	351.61	0.06	351.3
Do....	25.0	8.3280	0.52	2927.73	351.56			

2, 4-DIMETHYLHEXANE

6-2-42...	25.0	11.0514	0.55	3654.85	330.71			
Do....	25.0	21.7718	1.09	7198.65	330.64	330.66	0.09	330.5
Do....	25.0	11.0743	0.55	3661.46	330.63			

3, 4-DIMETHYLHEXANE

6-3-42...	25.0	10.6941	0.54	3649.51	341.26			
Do....	25.0	23.0734	1.05	7873.32	341.23	341.23	0.07	341.16
Do....	25.0	10.7099	0.54	3654.29	341.21			

BENZENE

6-4-42...	25.0	10.4328	0.52	4522.37	433.48			
Do....	25.0	29.7534	.90	12897.76	433.49	433.47	0.20	433.27
Do....	25.0	10.4071	.52	4510.91	433.45			

TOLUENE

6-25-42...	25.0	10.9906	0.55	4532.32	412.38			
Do....	25.0	39.9437	1.00	16473.38	412.42	412.41	0.15	412.2
Do....	25.0	9.9466	0.50	4102.42	412.44			

m-XYLENE

7-2-42...	25.0	15.3494	0.51	6165.02	401.65			
Do....	25.0	24.4975	.82	9842.57	401.78	401.77	0.02	401.7
Do....	25.0	15.3858	.51	6183.12	401.87			

o-XYLENE

7-3-42...	25.0	7.0353	0.50	2878.98	409.22			
Do....	25.0	7.2579	.81	2968.59	409.02	409.10	0.03	409.07
Do....	25.0	7.0666	.51	2890.60	409.05			

TABLE 1. *Results of vaporization experiments*—Continued

p-XYLENE

Date	Temperature	Mass	Evaporation rate	Net energy	γ	Mean γ_{25}	β_{25}	L_{25}
	°C	g	g/minute	int. j	int. j/g	int. j/g	int. j/g	int. j/g
8-6-42...	25.0	7.0780	0.51	2825.44	399.19	399.14	0.03	399.11
Do....	25.0	7.1573	.80	2856.82	399.15			
Do....	25.0	6.9596	.50	2777.38	399.07			

ETHYLBENZENE (IMPURE)

8-7-42...	25.0	14.8916	1.00	5922.79	397.73	397.72	0.05	(<397.67)
Do....	25.0	10.0133	0.50	3982.32	397.70			

ETHYLBENZENE (PURE)

8-15-42...	25.0	9.9914	0.50	3976.36	397.98	397.94	0.05	397.89
Do....	25.0	9.9927	.50	3976.08	397.90			

n-PROPYLBENZENE

8-8-42...	25.0	9.2470	0.46	3556.71	384.63	384.59	0.01	384.58
Do....	25.0	9.2387	.46	3552.74	384.55			

ISOPROPYLBENZENE

8-14-42...	25.0	11.1185	0.46	4175.61	375.56	375.55	0.02	375.53
Do....	25.0	13.5376	.68	5083.95	375.54			
Do....	25.0	9.4714	.95	3557.09	375.56			

1,3,5-TRIMETHYLBENZENE

8-17-42...	25.0	12.5212	0.25	4942.98	394.77	394.92	0.01	394.91
Do....	25.0	12.5059	.25	4940.82	395.08			

1,2,4-TRIMETHYLBENZENE

8-20-42...	25.0	9.9248	0.50	3958.02	398.80	398.78	0.01	398.77
Do....	25.0	9.9241	.50	3957.40	398.77			

1,2,3 TRIMETHYLBENZENE

8-23-42...	25.0	5.6214	0.11	2294.45	408.16	408.12	0.01	408.11
Do....	25.0	6.0106	.12	2452.78	408.08			

2,3,5-TRIMETHYLHEXANE

8-24-42...	25.0	10.1306	0.51	3271.76	322.96	322.95	0.04	322.91
Do....	25.0	10.1552	1.02	3279.28	322.92			
Do....	25.0	10.0867	0.51	3257.71	322.97			

* Sample of lower purity.

TABLE 1. *Results of vaporization experiments*—Continued

2,2,5-TRIMETHYLHEXANE

Date	Temperature	Mass	Evaporation rate	Net energy	γ	Mean γ_{25}	β_{25}	L_{25}
	°C	g	g/minute	int. j	int. j/g	int. j/g	int. j/g	int. j/g
7-27-42...	25.0	10.4036	0.52	3259.14	313.27	313.22	0.04	313.18
Do....	25.6	10.0603	1.01	3150.79	313.19			
Do....	25.0	10.0192	0.52	3137.91	313.19			

3-ETHYLPENTANE

7-28-42...	25.0	8.9272	0.45	3139.44	351.67	351.65	0.16	351.49
Do....	25.0	9.8908	.99	3480.02	351.63			

2,4-DIMETHYLPENTANE

7-30-42...	25.0	10.3614	0.50	3403.05	328.44	328.44	0.25	328.17
Do....	25.0	9.9658	1.00	3273.15	328.44			
Do....	25.0	9.0134	0.50	2960.38	328.44			

2,3-DIMETHYLBUTANE

7-31-42...	25.0	3.8323	0.48	1297.46	338.56	338.50	0.61	337.89
Do....	25.0	4.3122	.48	1459.45	338.45			

HEXAMETHYLETHANE (SOLID)

8-5-42...	25.0	2.4090	0.08	908.03	376.93	375.67	.....	375.6 ±2% (heat of sublimation)
Do....	25.0	1.6069	.08	601.64	374.41			

WATER

8-11-42...	25.0	6.3607	0.21	15536.4	2442.56	2442.05	0.06	2441.99
Do....	25.0	6.3691	.21	15550.6	2441.57			
Do....	.....	6.3694	.21	15554.2	2442.02			

The value of gamma, γ, given in column 6, is obtained by division of the value of net energy (col. 5) by the mass (col. 3). This quantity, gamma, γ, is greater than the latent heat of vaporization by the quantity beta, β, as described previously [1] in the method. In algebraic form,

$$L=\gamma-\beta.$$

The quantity β, which is very small in most of the experiments, is calculated from the relation

$$\beta=Tv\,dp/dT$$

where T is absolute temperature, v is specific volume of the liquid, and dp/dT is the vapor pressure slope. Values of vapor pressure slope and

liquid specific volume were calculated from data given in various sources [14, 15]. As the quantity β is small, high accuracy was not required in the source data. Calculated values of β are listed in column 8, and the derived values of heat of vaporization are listed in column 9.

Inspection of table 1 shows some duplication of experiments with a few materials. This was due either to an investigation of the effect of various drying methods, or to the availability of a purer sample at a later date. Ethylbenzene and 2,3-dimethylpentane are examples of the latter, and values of heats of vaporization on both samples of different purity are given to show the small effect on the result. The differences are less than 0.1 percent. The hydrocarbons 2,2-dimethylbutane and *trans*-1,4-dimethylcyclohexane were chosen to investigate the different drying methods. The results using different drying methods agreed to better than 0.01 percent.

Measurements on the heat of vaporization of water were made before, during, and after the series of hydrocarbon experiments. This procedure served as an additional check on the accuracy of the results. The average of the 15 water experiments gave a value of heat of vaporization at 25° C of 2441.37 int. j/g as compared to 2441.40 obtained with an earlier calorimeter [4]. The average deviation from this earlier value was 0.015 percent.

6. Accuracy of Results on Heat of Vaporization

In view of the purity of the hydrocarbons, smallness of heat leaks, and the excellent agreement of the resulting heats of vaporization of water with those with a different calorimeter, it is believed unlikely that the error in the heats of vaporization of the hydrocarbons listed in table 1 is more than 0.1 percent. In the case of hexamethylethane, experimental difficulties due to the fact that the material was a solid at 25° C lead to an estimated probable error of about 2 percent in the observed heat of sublimation.

III. Heat Capacity of Twelve Hydrocarbons

1. Introduction

In addition to the measurements of heat of vaporization, measurements of liquid heat capacity were undertaken, first in the temperature range 10° to 35° C, and later 5° to 45° C. After the first 12 hydrocarbons, however, the heat capacity measurements were discontinued to expedite the measurements on heat of vaporization.

The samples of hydrocarbons used in these measurements were the same as those used in the measurements of heat of vaporization. The apparatus was also the same, although the experimental procedure was quite different.

2. Method

As described in previous publications [2, 3, 4] the method consists of heating the calorimeter with a sample of saturated fluid over a measured temperature range. By making two types of experiments, one with a small amount of liquid in the calorimeter (low filling) and the other with a large amount of liquid in the calorimeter (high filling), it is possible to account for the tare heat capacity of the calorimeter and to obtain the change of a quantity denoted by alpha, α, which is a characteristic property of the fluid.

If Q_H and Q_L denote the measured quantities of heat added in the high and low filling experiments having masses of fluid M_H and M_L respectively, to heat the calorimeter from temperature T_1 to T_2, then it has been shown [1] that

$$Q_H = [Z]_1^2 + M_H[\alpha]_1^2,$$

$$Q_L = [Z]_1^2 + M_L[\alpha]_1^2,$$

where Z denotes a quantity that includes all energies that are independent of the amount of fluid in the calorimeter. Then,

$$Q_H - Q_L = [M_H - M_L][\alpha]_1^2,$$

or

$$\Delta\alpha = \Delta Q/\Delta M,$$

or

$$\Delta\alpha/\Delta T = \Delta Q/\Delta T\Delta M.$$

In other words, the change in the characteristic quantity, α, in a given temperature interval is merely the difference in the heat required in the high and low filling experiments, divided by the difference in the mass of fluid in the calorimeter in the two experiments.

It has also been shown [1] that the quantity α is related to the well known enthalpy, H, by the relation

$$H=\alpha+\beta.$$

where

$$\beta=Lv/(v'-v)=Tv\ dp/dT$$

where v' and v are the specific volumes of the saturated vapor and liquid, respectively, L the heat of vaporization, T the absolute temperature, and dp/dT the vapor pressure slope. At the temperatures of the present experiments, the term β is quite small compared to α so that the value of α is within a few parts in a thousand of the value of H. The value of $\Delta H/\Delta T$ for a given temperature interval is

$$\Delta H/\Delta T=\Delta\alpha/\Delta T+\Delta\beta/\Delta T,$$

and the value of dH/dT along the saturation path is derived by applying a correction for curvature of the enthalpy function.

The calculation of $C_{sat.}$, the heat capacity of the liquid along the saturation path, from the values of $(dH/dT)_{sat.}$ is performed by using the fundamental definitions of H and $C_{sat.}$.

$$(dH/dT)_{sat.}=dE/dT+p\ dv/dT+v\ dp/dT,$$

$$C_{sat.}=(dQ/dT)_{sat.}=dE/dT+p\ dv/dT.$$

Hence

$$C_{sat.}=(dH/dT)_{sat.}-v\ dp/dT=(dH/dT)_{sat.}-\beta/T.$$

In the temperature and pressure range of these experiments, the values of $C_{sat.}$ are very close to the values of $C_p=1$ atm, probably within 0.2 percent. If desired, the value of C_p may be calculated from the relation

$$C_{p=1}=C_{sat.}+\beta/T+T\ d^2v/dT^2(p-1)-dp/dT\ dH/dp,$$

where p is expressed in atmospheres. Accurate knowledge of specific volume is necessary in order to evaluate the factor d^2v/dT^2.

3. Experimental Procedure

The experimental procedure in the heat capacity experiments was very similar to that with the vaporization experiments. The sample in the calorimeter was brought to equilibrium at the desired starting temperature, and its temperature observed as noted in sections I and II. Measured electrical power was put into the calorimeter heater to heat the calorimeter at a rate of very close to ½ deg per minute. At the same time, the power inputs to the envelope heaters, the throttle heater, and the reference block heater were carefully regulated. The reference block heater current was regulated manually, so that the reference block temperature was always very close to the calorimeter temperature. The throttle heater was regulated automatically, as in section I, so that the temperature of the throttle was high enough to prevent any part of the tube from becoming colder than the temperature of the vapor in the calorimeter. This precaution was necessary to avoid condensation in the tube. The envelope heaters were regulated as previously described, partly automatic and partly manual.

After the calorimeter had heated the desired amount (either 5 or 10 degrees), the calorimeter power was turned off and the calorimeter allowed to come to equilibrium, as indicated by thermoelements located on the calorimeter. Because of the effectiveness of the heat distributing system in the calorimeter, the time to come to equilibrium was only a few minutes. Usually about 10 minutes was allowed, which was considerably longer than necessary, judging from the thermoelement readings. The temperature of the calorimeter was then observed as before, and a new heating period started. Measurements of heat leak coefficients (envelope, throttle, and residual) were made as in section II, except that the residual heat leak was checked only at the beginning and end of a series of heat capacity measurements.

4. Results of Heat-Capacity Experiments

The results of the heat-capacity experiments are given in table 2. Column 2 gives the mass of fluid in the calorimeter in the experiments for the data listed. The corresponding heat of vaporization experiments in table 1 were made after the high-filling experiments and before the low-filling experiments. Column 3 indicates the type of heat function for which corresponding values are listed in columns 4 to 8 for the various temperature intervals covered by the experiments. For example, the low-filling experiments with n-heptane on Nov. 22, 1941 gave for the temperature interval 20° to 25° C, a value of $Q/\Delta T$ of 81.21 int. j/deg.

TABLE 2. *Results of heat-capacity experiments*

Date	Mass	Heat function	(Int. j/g or int. j/g−°C				
			10° to 15°	15° to 20°	20° to 25°	25° to 30°	30° to 35°
WATER							
	g						
11-7-41	91.6182	$Q/\Delta T$	451.65	451.42	451.36	451.45	451.39
11-8-41	91.6182	$Q/\Delta T$		451.46	451.68	451.54	451.64
11-12-41	11.4744	$Q/\Delta T$	116.02	116.38	116.68	117.03	117.20
		$\Delta\alpha/\Delta T$ (observed)	4.1878	4.1807	4.1780	4.1732	4.172
		$\Delta\alpha/\Delta T$ (1939—calculated)	4.1868	4.1812	4.1778	4.1751	4.173
		Observed—calculated	+0.0010	−0.0005	+0.0005	−0.0019	−0.000
***n*-HEPTANE**							
11-19-41	59.4754	$Q/\Delta T$	198.70	200.03	201.38	202.72	204.10
Do	59.4754	$Q/\Delta T$	198.66	200.03	201.33	202.69	204.05
11-22-41	5.5453	$Q/\Delta T$	80.38	80.78	81.21	81.61	82.05
11-24-41	5.5453	$Q/\Delta T$	80.32	80.74	81.16	81.61	82.02
		$\Delta\alpha/\Delta T$	2.1941	2.2116	2.2283	2.2454	2.263
		$\Delta\beta/\Delta T$	0.0037	0.0046	0.0058	0.0068	0.008
		$\Delta H/\Delta T$	2.1978	2.2162	2.2341	2.2522	2.272
		$C_{sat.}$ (observed)	2.1975	2.2159	2.2337	2.2517	2.270
		$C_{sat.}$ (1939—calculated)	2.1980	2.2160	2.2344	2.2531	2.272
		Observed—calculated	−0.0005	−0.0001	−0.0007	−0.0014	−0.001
2,2,4-TRIMETHYLPENTANE							
12-4-41	61.1512	$Q/\Delta T$	192.27	193.81	195.41	196.97	198.58
12-5-41	61.1512	$Q/\Delta T$	192.24	193.77	195.37	196.95	198.58
12-5-41	61.1512	$Q/\Delta T$	192.25	193.79	195.41	197.00	198.62
12-9-41	7.4313	$Q/\Delta T$	83.13	83.61	84.05	84.51	85.00
Do	7.4313	$Q/\Delta T$	83.21	83.64	84.12	84.57	85.03
		$\Delta\alpha/\Delta T$	2.0307	2.0507	2.0721	2.0929	2.114
		$\Delta\beta/\Delta T$	0.0038	0.0046	0.0055	0.0067	0.007
		$\Delta H/\Delta T$	2.0345	2.0553	2.0776	2.0996	2.122
		$C_{sat.}$ (observed)	2.0342	2.0550	2.0772	2.0991	2.121
		$C_{sat.}$ (calculated)	2.0341	2.0553	2.0770	2.0991	2.121
		Observed—calculated	+0.0001	−0.0003	+0.0002	0.0000	0.000
***n*-OCTANE**							
12-13-41	49.4233	$Q/\Delta T$	175.57	176.65	177.74	178.66	180.03
12-15-41	49.4233	$Q/\Delta T$	175.57	176.65	177.77	178.87	180.01
12-17-41	5.1301	$Q/\Delta T$	79.06	79.38	79.76	80.12	80.47
12-18-41	5.1301	$Q/\Delta T$	79.08	79.44	79.76	80.11	80.46
		$\Delta\alpha/\Delta T$	2.1787	2.1954	2.2124	2.2272	2.2437
		$\Delta\beta/\Delta T$	0.0013	0.0017	0.0021	0.0025	0.0030
		$\Delta H/\Delta T$	2.1800	2.1971	2.2145	2.2297	2.2467
		$C_{sat.}$ (observed)	2.1799	2.1970	2.2144	2.2295	2.2463
		$C_{sat.}$ (calculated)	2.1804	2.1964	2.2134	2.2314	2.2486
		Observed—calculated	−0.0005	+0.0006	+0.0010	−0.0019	+0.0001
2-METHYLHEPTANE							
12-23-41	48.4561	$Q/\Delta T$	171.97	173.15	174.38	175.51	176.74
Do	48.4561	$Q/\Delta T$	172.00	173.19	174.38	175.61	176.82
1-3-42	2.7255	$Q/\Delta T$	73.58	73.90	74.23	74.60	74.92
		$\Delta\alpha/\Delta T$	2.1518	2.1708	2.1900	2.2077	2.2274
		$\Delta\beta/\Delta T$	0.0018	0.0023	0.0029	0.0036	0.0043
		$\Delta H/\Delta T$	2.1536	2.1731	2.1929	2.2113	2.2317
		$C_{sat.}$ (observed)	2.1535	2.1730	2.1927	2.2111	2.2314
		$C_{sat.}$ (calculated)	2.1536	2.1729	2.1923	2.2117	2.2312
		Observed-calculated	−0.0001	+0.0001	+0.0004	−0.0006	+0.0002

TABLE 2. *Results of heat-capacity experiments*—Continued

Date	Mass	Heat function	(Int. J/g or int. J/g−°C) 10° to 15°	15° to 20°	20° to 25°	25° to 30°	30° to 35°
3-METHYLHEPTANE							
[illegible]-2-42	48.8831	$Q/\Delta T$	172.04	173.25	174.45	175.64	176.90
Do	48.8831	$Q/\Delta T$	172.16	173.34	174.52	175.74	176.94
[illegible]-42	2.8493	$Q/\Delta T$	73.80	74.13	74.45	74.81	75.10
		$\Delta\alpha/\Delta T$	2.1354	2.1542	2.1731	2.1914	2.2119
		$\Delta\beta/\Delta T$	0.0017	0.0022	0.0027	0.0034	0.0041
		$\Delta H/\Delta T$	2.1371	2.1564	2.1758	2.1948	2.2160
		$C_{sat.}$ (observed)	2.1370	2.1563	2.1756	2.1946	2.2157
		$C_{sat.}$ (calculated)	2.1372	2.1560	2.1754	2.1952	2.2155
		Observed-calculated	−0.0002	+0.0003	+0.0002	−0.0006	+0.0002
4-METHYLHEPTANE			5° to 15° C	15° to 25° C	25° to 30° C	35° to 45° C	
[illegible]-42	49.0380	$Q/\Delta T$	172.02	174.72	177.27	179.84	
Do	49.0380	$Q/\Delta T$	172.26	174.77	177.30	179.84	
[illegible]-42	2.9001	$Q/\Delta T$	73.90	74.57	75.24	75.90	
		$\Delta\alpha/\Delta T$	2.1293	2.1712	2.2117	2.2528	
		$\Delta\beta/\Delta T$	0.0033	0.0051	0.0078	0.0114	
		$\Delta H/\Delta T$	2.1326	2.1763	2.2195	2.2642	
		$C_{sat.}$ (observed)	2.1325	2.1761	2.2192	2.2638	
		$C_{sat.}$ (calculated)	2.1326	2.1758	2.2195	2.2637	
		Observed-calculated	−0.0001	+0.0003	−0.0003	+0.0001	
2-5-DIMETHYLHEXANE							
[illegible]-42	45.9489	$Q/\Delta T$	164.79	167.22	169.78	172.15	
Do	45.9489	$Q/\Delta T$	164.90	167.30	169.70	172.16	
[illegible]-42	45.9489	$Q/\Delta T$	164.72	167.18	169.64	172.16	
[illegible]-42	2.8539	$Q/\Delta T$	73.72	74.46	75.12	75.94	
Do	2.8539	$Q/\Delta T$	73.82	74.53	75.22	75.89	
		$\Delta\alpha/\Delta T$	2.1124	2.1519	2.1937	2.2353	
		$\Delta\beta/\Delta T$	0.0046	0.0071	0.0106	0.0152	
		$\Delta H/\Delta T$	2.1170	2.1590	2.2043	2.2485	
		$C_{sat.}$ (observed)	2.1169	2.1588	2.2039	2.2479	
		$C_{sat.}$ (calculated)	2.1167	2.1594	2.2033	2.2481	
		Observed-calculated	+0.0002	−0.0006	+0.0006	−0.0002	
***n*-NONANE**							
[illegible]-42	58.8662	$Q/\Delta T$		197.36	199.84	202.45	
Do	58.8662	$Q/\Delta T$	194.99	197.45	199.92	202.49	
[illegible]-42	2.8269	$Q/\Delta T$	73.68	74.34	74.92	75.49	
Do	2.8269	$Q/\Delta T$	73.70	74.39	74.98	75.53	
		$\Delta\alpha/T$	2.1646	2.1956	2.2283	2.2656	
		$\Delta\beta/\Delta T$	0.0008	0.0014	0.0023	0.0037	
		$\Delta H/\Delta T$	2.1654	2.1970	2.2316	2.2693	
		$C_{sat.}$ (observed)	2.1654	2.1970	2.2316	2.2693	
		$C_{sat.}$ (calculated)	2.1654	2.1970	2.2316	2.2693	
		Observed-calculated	0.0000	0.0000	0.0000	0.0000	

TABLE 2. *Results of heat-capacity experiments*—Continued

Date	Mass	Heat function	(Int. J/g or int. J/g—°C				
			10° to 15°	15° to 20°	20° to 25°	25° to 30°	30° to
		n-DECANE					
2-8-42	23.8402	$Q/\Delta T$	119.08	120.34	121.58		
2-12-42	2.8086	$Q/\Delta T$	73.65	74.29	74.84		
		$\Delta\alpha/\Delta T$	2.1601	2.1896	2.2224		
		$\Delta\beta/\Delta T$	0.0003	0.0005	0.0009		
		$H/\Delta T$	2.1604	2.1901	2.2233		
		$C_{sat.}$ (observed)	2.1604	2.1901	2.2233		
		$C_{sat.}$ (calculated)	2.1604	2.1900	2.2234		
		Observed-calculated	0.0000	+0.0001	−0.0001		
		2,3,4-TRIMETHYLPENTANE					
2-14-42	45.6731	$Q/\Delta T$	163.47	165.85	168.42		
2-17-42	2.8326	$Q/\Delta T$	73.61	74.32	75.04		
		$\Delta\alpha/\Delta T$	2.0975	2.1365	2.1797		
		$\Delta\beta/\Delta T$	0.0039	0.0061	0.0090		
		$\Delta H/\Delta T$	2.1014	2.1426	2.1887		
		$C_{sat.}$ (observed)	2.1012	2.1423	2.1883		
		$C_{sat.}$ (calculated)	2.1011	2.1427	2.1879		
		Observed-calculated	+0.0001	−0.0004	+0.0004		
		2,3,3-TRIMETHYLPENTANE					
2-19-42	55.2225	$Q/\Delta T$	182.95	185.41	188.25		
2-21-42	2.8401	$Q/\Delta T$	73.50	74.22	74.91		
		$\Delta\alpha/\Delta T$	2.0894	2.1227	2.1637		
		$\Delta\beta/\Delta T$	0.0038	0.0058	0.0086		
		$\Delta H/\Delta T$	2.0932	2.1285	2.1723		
		$C_{sat.}$ (observed)	2.0929	2.1281	2.1718		
		$C_{sat.}$ (calculated)	2.0926	2.1290	2.1709		
		Observed-calculated	+0.0003	−0.0009	+0.0009		
		WATER					
2-24-42	51.5136	$Q/\Delta T$	283.96	284.04	284.37		
2-25-42	51.5136	$Q/\Delta T$	284.00	284.04	284.36		
2-27-42	4.4432	$Q/\Delta T$	86.62	87.18	87.76		
Do	4.4432	$Q/\Delta T$	86.47	86.98	87.49		
		$\Delta\alpha/\Delta T$ (observed)	4.1888	4.1788	4.1741		
		$\Delta\alpha/\Delta T$ (1939-calculated)	4.1910	4.1794	4.1744		
		Observed-calculated	−0.0022	−0.0006	−0.0003		
		3,3-DIMETHYLHEXANE					
3-6-42	57.3524	$Q/\Delta T$	187.75	190.79	193.77		
3-11-42	57.3524	$Q/\Delta T$	187.45	190.56	193.53		
Do	57.3524	$Q/\Delta T$	187.40	190.44	193.45		
3-14-42	3.8482	$Q/\Delta T$	75.99	76.64	77.37		
3-16-42	3.8482	$Q/\Delta T$	75.95	76.65	77.36		
3-16-42	3.8482	$Q/\Delta T$	75.83				
		$\Delta\alpha/\Delta T$	2.0860	2.1298	2.1721		
		$\Delta\beta/\Delta T$	0.0042	0.0064	0.0095		
		$\Delta H/\Delta T$	2.0902	2.1362	2.1816		
		$C_{sat.}$ (observed)	2.0901	2.1360	2.1813		
		$C_{sat.}$ (calculated)	2.0903	2.1353	2.1820		
		Observed-calculated	−0.0002	+0.0007	−0.0007		

The values of $Q/\Delta T$ thus listed in table 2 are calculated from the electrical energy input during the experiment, corrected for the three heat leaks described in section II and for the departures of the beginning and end temperatures of the experiment from the desired even temperature. As in the vaporization experiments, the arithmetical sum of the heat leaks for an average experiment was about 1 or 2 joules, most of which was caused by regulating the temperature of the upper tube above the temperature of the calorimeter to avoid condensation. The heat leak on most experiments contributed only about 0.2 percent to the energy input, and even this small amount was effectively eliminated differentially by the experimental procedure that gave the same heat leak conditions in the high-filling experiments as in the low-filling experiments.

The beginning and end temperatures of the calorimeter in the heat capacity experiments were usually regulated to within a few hundredths of a degree of the desired even temperatures so that the resultant corrections applied to the measured $Q/\Delta T$ amounted to less than 1 percent. As the heat capacity of the calorimeter and contents is known from the experiments, these corrections should introduce no significant error in the results.

The values of $\Delta\alpha/\Delta T$ listed in table 2 are obtained by dividing the difference between the average values of $Q/\Delta T$ for the high-filling experiment and corresponding average values of $Q/\Delta T$ for the low-filling experiment, by ΔM, the difference in the masses of fluid in the calorimeter in the high and low-filling experiments. Values of $\Delta H/\Delta T$ are calculated from $\Delta\alpha/\Delta T$ by adding $\Delta\beta/\Delta T$ calculated from specific volume and vapor pressure data as described under Method. Values of $C_{sat.}$ at the mid temperatures of the intervals are calculated from $\Delta H/\Delta T$ by first applying a curvature correction to get dH/dT at the mid temperature of the intervals, and then subtracting values of β/T. All these corrections are small, so that the resulting values of $C_{sat.}$ do not differ from the $\Delta\alpha/\Delta T$ by more than a few parts per thousand.

In order to "smooth" the data, an equation of the form $C_{sat.}=A+BT+CT^2$ was fitted to the data for each material by the method of least squares. Table 3 gives the constants of the equation for the 12 hydrocarbons as well as values at 5-degree intervals in the experimental range as calculated from these equations. The values of $C_{sat.}$ (calculated) listed in table 2 are also computed from these equations in order to judge the accidental variations in the experimental values of heat capacities. It was found that the average deviation of a determination of heat capacity from the value calculated from the equation was 0.011 percent for the 10-degree intervals and 0.022 percent for the 5-degree intervals.

Similar to the vaporization experiments, heat capacity experiments with water were made at the beginning of this series of measurements and near the end, as a check on the accuracy of the results. It was found that the 30 experiments with water gave an average difference of $\Delta\alpha/\Delta T$ of about 0.025 percent from the values reported with another calorimeter [4].

In addition to the check on the values of heat capacity of water, it was possible to also check on values of the heat capacity of *n*-heptane as determined in the same large calorimeter [4] as was used for water. These unpublished determina-

TABLE 3. *Values of smoothed heat capacities*

Material	Equation constants			C_{sat} (int. J/g° C)								
	A	$10^3 B$	$10^6 C$	5°	10°	15°	20°	25°	30°	35°	40°	45°
2-methylheptane	2.10547	3.840	0.853		2.1440	2.1632	2.1826	2.2020	2.2214	2.2409		
3-methylheptane	2.09208	3.490	9.425		2.1279	2.1466	2.1657	2.1852	2.2053	2.2258		
4-methylheptane	2.08990	4.245	2.500	2.1112	2.1326	2.1541	2.1758	2.1976	2.2195	2.2415	2.2637	2.2860
2,5-Dimethylhexane	2.07498	4.119	5.248	2.0957	2.1167	2.1379	2.1594	2.1812	2.2033	2.2256	2.2481	2.2710
3,3-Dimethylhexane	2.04712	4.234	8.750	2.0685	2.0903	2.1126	2.1353	2.1584	2.1820	2.2060	2.2305	2.2554
2,2,4-Trimethylpentane	1.98314	3.958	9.419		2.0237	2.0425	2.0661	2.0880	2.1104	2.1332		
2,3,4-Trimethylpentane	2.06320	3.603	18.500	2.0817	2.1011	2.1214	2.1427	2.1648	2.1879	2.2120	2.2369	2.2628
2,3,3-Trimethylpentane	2.06192	2.786	28.250	2.0766	2.0926	2.1101	2.1290	2.1492	2.1709	2.1941	2.2186	2.2445
n-Heptane	2.15453	3.396	6.791	2.1717	2.1892	2.2070	2.2252	2.2437	2.2625	2.2817	2.3012	2.3211
n-Octane	2.14441	2.637	19.140		2.1727	2.1883	2.2048	2.2223	2.2407	2.2602		
n-Nonane	2.13688	2.700	15.250	2.1508	2.1654	2.1808	2.1970	2.2139	2.2316	2.2501	2.2693	2.2893
n-Decane	2.13450	2.407	18.500	2.1470	2.1604	2.1748	2.1900	2.2062	2.2234	2.2414	2.2604	2.2803

tions were made in 1939 by Osborne, Stimson, and Ginnings with a sample of *n*-heptane furnished by D. B. Brooks of this Bureau. Three series of low-filling experiments were made over the temperature range 5° to 100° C, but only one series of high-filling experiments was completed in the range 5° to 90° C on account of interruption of the experiments by a mechanical breakdown.

The results of the 1939 measurements on *n*-heptane are given in table 4. Columns 2 and 3 give the net energy inputs for the low- and high-filling experiments, having 85.859 and 743.123 g of heptane, respectively. These values of net energy include heat leak correction and corrections for [illegible] temperatures. The values of $\Delta\alpha/\Delta T$ in colum[n] were obtained by dividing the difference in [e]nergies for the high and low fillings by the pro[d] of the difference in mass of heptane (657.264) ti[mes] the number of degrees in the temperature inter[val]. The values of β/T in column 8 and $\Delta\beta/\Delta T$ column 5 were calculated from liquid spec[ific] volume data in the International Critical Ta[bles] [13] and vapor pressure data from the tables of t[he] American Petroleum Institute Project 44 [1[4]] and from Willingham et al. [16].

The values of $C_{sat.}$ were calculated from $\Delta\alpha$ [illegible]

TABLE 4. *Results of 1939 n-heptane heat capacity experiments*

Temperature interval	Net energy (Q)		$\Delta\alpha/\Delta T$	$\Delta\beta/\Delta T$	$\Delta H/\Delta T$	$4H/dT$	β/T	$C_{sat.}$ (observed)	$C_{sat.}$ (calculated)	(Ob-served) minus (calculated)
	Low filling	High filling								
°C	*int. j*	*int. j*	*int. j/g−°C*	*int. j/g−°C*	*int. j/g−°C*	*int. j/g−°C*	*int. j/g−°C*	*int. j/g−°C*	*int. j/g−°C*	*Per cent*
5 to 10	1787.8	8939.7	2.1763	0.0030	2.1793	2.1793	0.0002	2.1791	2.1804	−0.06
10 to 20	3612.8	18,102.1	2.2045	.0042	2.2087	2.2086	.0003	2.2083	2.2070	.06
20 to 30	3665.2	18,381.2	2.2390	.0062	2.2452	2.2451	.0004	2.2447	2.2437	.04
30 to 40	3724.2	18,662.8	2.2728	.0089	2.2817	2.2816	.0007	2.2809	2.2817	−.04
40 to 50	3789.0	18,972.1	2.3100	.0124	2.3224	2.3223	.0010	2.3213	2.3211	.01
50 to 60	3857.3	19,276.3	2.3459	.0167	2.3626	2.3625	.0014	2.3611	2.3619	−.03
60 to 70	3930.7	19,588.9	2.3838	.0222	2.4060	2.4059	.0019	2.4040	2.4040	.00
70 to 80	4008.4	19,924.3	2.4215	.0288	2.4503	2.4502	.0026	2.4476	2.4474	.01
80 to 90	4094.4	20,259.2	2.4594	.0365	2.4959	2.4958	.0034	2.4924	2.4923	.00

by the method used in table 2. An equation of the type $C_{sat.}=A+BT+CT^2$ was fitted to the observed values of $C_{sat.}$ listed in table 4, giving values of the constants as $A=2.15453$, $B=.0033961$, and $C=6.7909\times10^{-6}$, when T is in degrees C and $C_{sat.}$ is in int. j/g-deg C. The average deviation of the 1939 observed values from the values calculated from this equation is 0.028 percent, whereas the average deviation of the 1941 observed values from this equation (based on the 1939 results) is 0.037 percent. A comparison of the observed values is given in figure 4.

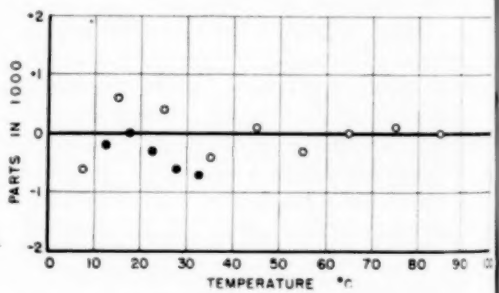

FIGURE 4. *Deviations of observed heptane heat capacities from formulation.*

○, 1939 observed; ●, 1941 observed.

5. Discussion of Accuracy of Heat Capacity Results

When the calorimeter was designed, it was not expected that it would give as accurate results in the heat capacity measurements as in the vaporization experiments. This was due to the small size of the calorimeter, which was a more important factor in the heat capacity experiments than in the vaporization experiments. However, [in] view of the excellent agreement of the values [of] heat capacity of water and heptane with value[s] obtained with a larger calorimeter at an earli[er] date, it is believed that the calorimeter is capabl[e] of better than 0.1 percent in heat capacities [in] spite of its small size. As some of the heat capac[i]ity results are based on scanty data, and som[e]

such as *n*-decane) involve smaller amounts of hydrocarbon in the calorimeter than others, it is believed that the error in the heat capacity results about 0.1 percent with most hydrocarbons such as *n*-heptane, but that it may be as large as 0.3 percent with a few hydrocarbons such as *n*-decane.

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IV. References

[1] N. S. Osborne, BS J. Research **4,** 609 (1930).
[2] N. S. Osborne, H. F. Stimson, and E. F. Fiock, BS J. Research **5,** 411 (1930).
[3] N. S. Osborne, H. F. Stimson, and D. C. Ginnings, J. Research NBS **18,** 389 (1937).
[4] N. S. Osborne, H. F. Stimson, and D. C. Ginnings, J. Research NBS **23,** 197 (1939).
[5] C. H. Meyers, BS J. Research **9,** 807 (1932).
[6] E. F. Mueller, Bul. BS **13,** 547 (1916) S288.
[7] A. F. Forziati, A. R. Glasgow, Jr., C. B. Willingham, and F. D. Rossini, J. Research NBS **36,** 129 (1946) RP1695.
[8] F. L. Howard, T. W. Mears, A. Fookson, P. Pomerantz, and D. B. Brooks, J. Research NBS **38,** 365 (1947).
[9] P. L. Cramer and M. J. Mulligan, J. Am. Chem. Soc. **58,** 373 (1936).
[10] J. Timmermans and F. Martin, J. Chem. Phys. **23,** 733 (1926).
[11] B. J. Mair and S. T. Schicktanz, J. Research NBS **11,** 665 (1933).
[12] A. R. Glasgow, Jr., C. B. Willingham, and F. D. Rossini, National Bureau of Standards. Unpublished.
[13] Elizabeth W. Aldrich, Ind. and Eng. Chem. **3,** 348 (1931).
[14] Tables of physical constants of selected hydrocarbons issued by the American Petroleum Institute Research Project 44.
[15] International Critical Tables 3 (McGraw-Hill Book Co., Inc., New York, N. Y., 1928).
[16] C. B. Willingham, W. J. Taylor, Joan M. Pignocco, and F. D. Rossini, J. Research NBS **35,** 219 (1945).

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